PB89-219968

Potential Technologies for Collection and Destruction of CFCs (Chlorofluorocarbons), Halons, and Related Compounds

Radian Corp., Austin, TX

Prepared for:

Environmental Protection Agency, Research Triangle Park, NC

Jul 89

U.S. Department of Commerce
National Technical Information Service
NTIS

PB89-219968

EPA/600/2-89/037
July 1989

POTENTIAL TECHNOLOGIES FOR COLLECTION AND DESTRUCTION OF CFCs, HALONS, AND RELATED COMPOUNDS

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EPA Contract 68-02-4286
Work Assignment Nos. 20 and 21

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NATIONAL TECHNICAL INFORMATION SERVICE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA *(Please read Instructions on the reverse before completing)*		
1. REPORT NO. EPA/600/2-89/037	2.	3. RECIPIENT'S ACCESSION NO. PB89 219968/AS
4. TITLE AND SUBTITLE Potential Technologies for Collection and Destruction of CFCs, Halons, and Related Compounds		5. REPORT DATE July 1989 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Kirk E. Hummel and Thomas P. Nelson		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Radian Corporation P. O. Box 201088 Austin, Texas 78720-1088		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. 68-02-4286, Tasks 20 and 21
12. SPONSORING AGENCY NAME AND ADDRESS **EPA, Office of Research and Development** Air and Energy Engineering Research Laboratory **Research Triangle Park, NC 27711**		13. TYPE OF REPORT AND PERIOD COVERED Final; 3/88 - 5/89 14. SPONSORING AGENCY CODE **EPA/600/13**

15. SUPPLEMENTARY NOTES AEERL project officer is Dale L. Harmon, Mail Drop 62B, 919/541-2429.

16. ABSTRACT The report gives recommendations of a multidisciplinary panel of experts on new or novel technologies (or modifications of existing technologies) which show the most promise for the collection and destruction of chlorofluorocarbons (CFCs) and related compounds. Panel members met in a 'roundtable' format to discuss their experiences and relate them to the compounds of interest. The panel identified technologies holding the most promise and suggested general areas of research and development needed to develop collection and destruction technologies.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Chlorohydrocarbons	Stationary Sources	07C
Fluorohydrocarbons	Chlorofluorocarbons	
Collection	Halons	14G
Destruction		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	**Unclassified**	98
	20. SECURITY CLASS *(This page)* **Unclassified**	22. PRICE MF PC 6/15.95/ 6.95

EPA Form 2220-1 (9-73)

ABSTRACT

The objective of this study was to assemble a multidisciplinary panel of experts to recommend new or novel technologies (or modifications of existing technologies) which show the most promise for the collection and destruction of chlorofluorocarbons (CFCs) and related compounds. The panel members met in a "roundtable" format to discuss their experiences and relate them to the compounds of interest. The panel identified which technologies held the most promise and made suggestions for general areas of research and development needed to develop collection and destruction technologies.

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SECTION 1

INTRODUCTION

BACKGROUND

A family of chemicals known as chlorofluorocarbons (CFCs) have been implicated in the depletion of stratospheric ozone. A number of adverse health and ecological effects could result from such depletion. For this reason a number of strategies or options for controlling the release of these compounds are being evaluated by governments and industry worldwide.

Existing technological means have not been conclusively demonstrated as suitable for curtailing CFC emissions from certain sources to acceptable levels. Because of their great chemical stability, CFCs are very difficult to break down. In order to be destroyed, the CFC would first have to be collected. Thus, EPA felt a program was needed to evaluate various existing and new or novel technologies for the collection and destruction of CFCs.

The Navy has the need for new or novel technology to remove and destroy toxic compounds which may be used in chemical warfare (CW). The current generation of shipboard CW defensive systems are based on activated carbon adsorption. These devices are considered effective against high molecular weight, low volatility chemicals such as "nerve agents" which are strongly adsorbed. However, in order to deal with high volatility, weakly adsorbed toxic compounds (such as hydrogen cyanide, HCN), a reactive impregnant has been added to the carbon. It is known that some CFCs are not strongly held on carbon, so it was assumed that if a technology could be developed for collection and/or destruction of CFCs, it might be possible to modify such a process for shipboard use as a CW defensive system.

To this end, the U.S. EPA and Navy proposed assembling a multi-disciplinary panel of experts to recommend new or novel technologies (or modifications of existing technologies) which show the most promise for future development. The panel would then meet in a "round-table" format to discuss the proposed technologies. This report presents the results of this meeting in the sections that follow.

Follow-up work is planned in FY89 to continue the development of CFC destruction technologies if funds are made available. The follow-up work will include a better definition of collection technologies for collection of dilute emissions of CFCs to allow more economical destruction. The research proposed by the expert panel will be reviewed by the U.S. EPA and Navy, and the highest priority projects will be selected for initiation in FY89 as funding permits. Future plans are to develop the ideas generated in the first phase for destruction of CFCs through small pilot scale evaluations and then adapt these technologies to the collection and destruction of chemical agents which may be used in chemical warfare.

OBJECTIVES

The objective of the expert panel was to comment on those technologies applicable to collection and destruction of CFCs and related compounds. The panel members discussed their experiences and related them to the compounds at hand. Also, they identified which technologies held the most promise and made suggestions for general areas of research and development needed to develop efficient collection and destruction technologies.

APPROACH

The CFC Destruction Expert Panel was comprised of persons with a wide variety of expertise. Radian Corporation served as the General Contractor, and contacted individuals with recognized ability in the area of waste collection and destruction. The members of the Expert Panel and their relevant area of expertise are listed in Table 1. It was hoped that at least one industrial

TABLE 1. LIST OF PARTICIPANTS

EXPERT PANEL

Dr. Barry Dellinger	University of Dayton Research Institute	Thermal Treatment
Mr. Jose Bravo	University of Texas	Separations
Mr. Don Matter	Rollins Environmental	Thermal Treatment
Mr. Don Oberacker	U.S. EPA/HWERL	Thermal Treatment
Mr. Garry Howell	U.S. EPA/HWERL	Chemical Treatment
Dr. Norman Plaks	U.S. EPA/AEERL	Corona Discharge
Mr. Joe McSorley	U.S. EPA/AEERL	Combustion Research
Mr. Ron Bell	Radian Corporation	Thermal Treatment
Dr. Frank Castaldi	Radian Corporation	Biological Treatment
Dr. David DeBerry	Radian Corporation	Chemical Treatment

VENDOR PARTICIPANTS

Dr. Hugh Reilly	Sandia National Laboratory	Solar Furnace
Ms. Kristine Snow	Ogden Environmental	Circulating Bed Combustor
Dr. Larry Britton	Texas Research Institute	Biological Treatment

OTHER PARTICIPANTS

Mr. Dale Harmon	U.S. EPA/AEERL
Dr. Dean Smith	U.S. EPA/AEERL
Mr. Bill Rhodes	U.S. EPA/AEERL
Mr. Roger Gibbs	U.S. Navy/NSWC
Mr. G.E. (Buzz) Harris	Radian Corporation
Mr. Tom Nelson	Radian Corporation
Mr. Kirk Hummel	Radian Corporation

chemist from a CFC producer would serve on the panel, but all three major U.S. producers (DuPont, Allied, and Pennwalt) declined to participate.

A "Workbook" containing background material and properties of the compounds of interest was prepared and provided to the members of the panel in advance of the meeting. Also, Radian contacted several commercial vendors of waste destruction technology and invited them to send a representative to discuss their processes (see also Table 1).

The actual panel meeting was held June 23 and 24, 1988 at the Woodfin Suites Hotel in Austin, TX. One of the vendor participants, Ogden Environmental, did not attend. The meeting agenda is shown in Table 2.

This report is intended to summarize the information presented at the meeting, and discuss the conclusions of the expert panel. The report is divided into the following sections:

- Introduction (containing Background, Objectives, and Approach);
- Summary and Recommendations of Expert Panel;
- Specific Research Tasks to Address Recommendations; and
- Conclusions.

The report also contains appended information on the meeting notes, handouts from the meeting, and relevant articles.

TABLE 2. FINAL AGENDA

June 23, 1988		
8:00AM	Welcome and Introductions	Mr. G.E. Harris
8:05AM	Opening Statement, U.S. EPA	Mr. Dale Harmon
8:15AM	Opening Statement, U.S. Navy	Mr. Roger Gibbs
8:25AM	Workbook Overview	Mr. Kirk Hummel
9:00AM	Expert Panel Commentary	Dr. Barry Dellinger
9:15AM	Expert Panel Commentary	Mr. Jose Bravo
9:30AM	Expert Panel Commentary	Mr. Don Matter
9:45AM	Expert Panel Commentary	Mr. Don Oberacker
10:00AM	Morning Break	
10:15AM	Expert Panel Commentary	Mr. Garry Howell
10:30AM	Expert Panel Commentary	Dr. Norman Plaks
10:45AM	Expert Panel Commentary	Mr. Joe McSorley
11:00AM	Expert Panel Commentary	Mr. Ron Bell
11:15AM	Expert Panel Commentary	Dr. Frank Castaldi
11:30AM	Expert Panel Commentary	Dr. David DeBerry
12:00N-1:30PM	Lunch Break	
1:30PM	Vendor Presentation	Dr. Hugh Reilly
2:00PM	Vendor Presentation	Ms. Kristine Snow
2:30PM	Afternoon Break	
2:45PM	Vendor Presentation	Dr. Larry Britton
3:15PM	"Hazcon" Video Presentation	
3:30PM-5:00PM	Open Discussion	
7:00PM	Dinner	
June 24, 1988		
8:00AM-10:00AM	Open Discussion	
10:00AM	Morning Break	
10:00AM-12:00N	Ranking of Technologies Discussion	
12:00N-1:30PM	Lunch Break	
1:30PM-3:30PM	Conclusions/Recommendations	

SECTION 2

SUMMARY AND RECOMMENDATIONS OF THE EXPERT PANEL

In order to address the issues for EPA and Navy in terms of their particular interests, it was decided that the expert panel should separately evaluate technologies for collection and for destruction of CFCs, halons, and CW agents. Therefore, proposed technologies were evaluated for two distinct classes:

- Technologies capable of collecting, removing, or destroying the compounds from the feed stream and providing an off-gas or effluent suitable for breathing air (for example, shipboard CW defense); and

- Technologies capable of collecting, removing, or destroying the compounds from the feed stream with no requirement for a breathable off-gas (for example, bulk incineration of contaminated CFCs).

The reasons for the division of technologies are fairly simple: the Navy is only interested in technologies that generate a breathable airstream. For collective protection systems used to filter large quantities of contaminated air entering through ventilation systems and for individual protection systems (gas masks), the cleansed airstream will be breathed by shipboard personnel.

The U.S. Environmental Protection Agency's main interest was to review the technologies that are most applicable to the destruction of fully halogenated materials such as chlorofluorocarbons and halons. Those materials are currently being regulated in the United States and elsewhere under the limits established in the Montreal protocol. The Montreal protocol also allows for production increases equal to any destruction of the regulated compound. To date, these destruction techniques have not been identified.

Technologies capable of providing both breathable and non-breathable gas are of interest to EPA. Although large volumes or high concentrations of CFCs might be most efficiently destroyed by a technology which would generate a non-breathable gas (e.g., incineration), CFC emissions from such sources as flexible foams or solvents might be considered for destruction or recovery by technologies which would generate breathable air and allow the air to be recycled to the work area or discharged directly to the environment.

SUMMARY OF EXPERT PANEL

The panel reviewed many technologies including thermal, chemical and biological processes. In most instances biological processes can only be used on dilute aqueous streams and the biological destruction rate will be very slow. This is based on experience with highly halogenated PCBs. Therefore, for the two applications at hand, biological processes were eliminated as possible candidates.

Breathable Air (CW Defensive Systems)

The overall conclusions of the expert panel for the breathable air situation was that the use of carbon adsorption as currently done by the Navy was the most reasonable, commercially available process. However, carbon adsorption is limited because high volatility toxic compounds are not strongly held on carbon, and the reactive impregnants which are added to remove these compounds are non-specific (they react with a host of other contaminants) and of limited capacity. Furthermore, there is currently no method to determine when the carbon needs to be replaced.

The potential candidates to replace the present carbon adsorption system are listed below:

- Inorganic Membranes; These may be either ceramic membranes or carbon molecular sieves. The current applications for ceramic membranes

are in the area of ultrafiltration, so they are not directly applicable to gas purification. Carbon molecular sieve membranes are being developed specifically for gas separations. Research into the materials science aspects of these structures (such as obtaining reduced pore diameters) could lead to development of sturdy, chemically resistant separation devices. In the same manner as other compounds such as silica, alumina, or magnesia, these inorganic membranes could also serve as supports for catalytic reaction.

- Chemical Scrubbing/Destruction; This technology includes the use of a highly alkaline, non-aqueous scrubbing liquor to absorb and destroy the compounds of interest. One example that was cited was the K-PEG process (KOH is the alkaline component; poly-ethylene glycol is the solvent). This process has been used to destroy PCBs, but has not been developed beyond the bench-scale.

- Corona Discharge; This process uses highly energized electrons from an ionized corona discharge to dissociate the compounds of interest. Early testing has included using a computer model to refine the geometry of the flow path to obtain higher destruction efficiency. Additional research and testing will be required to determine the energy requirements and obtain results on other compounds. One advantage of this process is that it operates at essentially ambient temperature and pressure.

- Metals Scrubbing; This technology uses an active metal such as zinc or aluminum to react with the compounds of interest. It is known that active metals can rapidly destroy halogenated organics such as PCBs. One advantage is that a solid salt may be formed (e.g., $ZnCl_2$) which can easily be removed. However, this process has not been successfully proven beyond the pilot-scale. Further research will need to address the problem of maintaining an active metal surface in the presence of air and moisture.

- New Adsorbents; This technology uses tailor-made adsorbents, such as new zeolites or aluminas, or new polymeric adsorbents, to obtain the desired separation. One advantage of this technology is that these compounds have a uniform or well-defined structure which results in more consistent performance. Also, their properties may be altered using various pretreatments.

Clearly there will be limitations since these technologies will likely be tested using a subset of the full spectrum of potential compounds. New compounds could be developed which might defeat these defenses.

Table 3 lists the expert panel's recommendations for those processes which appear to offer the greatest potential for successful application to the breathable air case. The listing is in alphabetical order. Listed in the table is a brief description of the process, potential waste streams to which it applies, stage of development, and its strengths and weaknesses. Additional discussion concerning other technologies not listed is contained in the Appendix (under Meeting Notes).

Non-breathable Air (CFC Destruction)

In the area of destruction of fully halogenated organics without the need of a breathable off-gas, current thermal destruction processes (i.e., incineration) may be adequate. Destruction of chlorofluorocarbon wastes is currently being done in at least one permitted facility (operated by Rollins Environmental Services). The harsh environment created by the hydrogen fluoride in the off-gas is one potential cause for concern, as specially designed internal firebrick and mortars may be required. For example, one company's experience (Rollins) led them to restrict the destruction of CFCs to one such specially designed incinerator.

TABLE 3. SUMMARY OF EXPERT PANEL RECOMMENDATIONS FOR BREATHABLE AIR CASE

Process Name	Description	Phase	Status	Expressed Advantages	Potential Limitations
BREATHABLE AIR (e.g., CW Defensive Systems)					
Carbon Adsorption	Current Practice	G,L	C	Simple technology proven track record	Requires periodic regeneration or replacement; requires impregnation for some high volatility chemicals
Inorganic membranes	Ceramic membranes or Carbon Molecular sieves	G,L	P	Operation at high temperatures, chemically resistant	May still require carbon bed downstream, or metallic salt impregnants to react with high volatility compounds
Chemical Scrubbing/ Destruction	Highly alkaline, non-aqueous scrubbing liquor	G	B	Superior to scrubbing alone, since equilibrium limitation is removed	Downstream treatment required to prevent contamination of carbon bed; may require pretreatment of inlet air to remove moisture
Corona Discharge	High voltage generates excited electrons which dissociate hazardous wastes	G	B	Destruction occurs at ambient temperatures, rapid process	May still require carbon bed downstream; requires high voltage power supply; may generate ozone and/or NO_x
Metals Scrubbing	Active metals such as zinc or aluminum	G,L	B,P	Rapid reaction forms salts (e.g., NaCl) which are easily removed	Uncertain ability to maintain active metal surface; may require pretreatment of inlet air to remove moisture
New Adsorbents	Tailor-made adsorbents, such as new zeolites or other aluminas, or polymeric adsorbents	G,L	(1)	Improvement over carbon with well-defined structure	New selective adsorbent bed could conceivably allow some less toxic compounds through to be handled by a cheap carbon bed instead of an expensive specialty adsorbent bed

G = Gaseous, L = Liquid, S = Solid, B = Bench-scale, P= prototype, C = Commercial

(1) Some zeolites are commercially available, although for the applications in this study additional research will probably be needed.

Although CFCs are currently being incinerated, there is very limited data regarding the destruction efficiency or products of incomplete combustion (PICs) resulting from these operations. Data is lacking regarding the quantity and fate of PICs; such compounds may be toxic and/or may pose a threat to stratospheric ozone.

To summarize the status of incineration of CFCs, this is the only demonstrated technology which is currently being used, and will likely continue to be used in the near term. However, the feared potential of corrosive attack to the refractory and the lack of accurate data on destruction efficiency and PICs are problems which require solutions.

Other potential technologies which were recommended as good candidates are listed below:

- Catalytic Thermal Destruction; Metal catalysts have been successfully used to destroy dilute hydrocarbon gas streams at reduced temperature, thereby saving energy and improving the economics of this control technology. Potential problems with the destruction of chlorinated hydrocarbons using this technology include low destruction efficiency due to catalyst deactivation. Catalytic processes may lose their advantage if high destructive efficiencies require high temperatures.

- Chemical Scrubbing/Destruction; This process has already been described for the breathable air case.

- Corona Discharge; This process has already been described for the breathable air case.

- Metals Scrubbing; This process has already been described for the breathable air case.

- Pyrolysis; This technology involves thermal treatment in the absence of air. Since CFCs are destroyed through bond homolysis or hydrolysis, simple heating without air is sufficient to break the bonds. Heating without air results in reduced gas flow, because only the waste decomposition gases are sent to the downstream scrubbers, in contrast to direct flame incineration where both waste decomposition gases and fuel combustion gases are treated. Capital and operating costs of the downstream treatment equipment for pyrolysis may be less than direct flame incineration because of the smaller size allowed by the reduced gas flow.

- Supercritical Water Oxidation (SCWO); This process is a modification of Wet Air Oxidation (WAO) (described below) which involves a supercritical fluid (water). This new technology features much higher reaction rates than those achievable in the well known WAO technology. Furthermore, SCWO operates at very high oxidant concentrations which enhances the kinetics and produces favorable equilibria. This technology could be limited by the metallurgy of the system.

- Wet Air Oxidation (WAO); This process uses a high temperature (> 300°C) aqueous stream and oxygen to destroy many organic compounds. Since CFCs do not contain a hydrogen atom or a double bond, they are expected to be resistant to oxidation. However, CFCs are susceptible to hydrolysis during incineration[1], so a high temperature aqueous treatment could be effective.

---

[1] R.F. Hein, DuPont Co. - Jackson Laboratory in DuPont's February 1980 Submission to EPA entitled "An Overview of Industry Efforts to Investigate the Potential for CFC Emission Reduction."

Table 4 lists the expert panel's recommendations for those processes which appear to offer the greatest potential for successful application to the breathable air and non-breathable air cases. The listing is in alphabetical order.

Listed in the table is a brief description of the process, potential waste streams to which it applies, stage of development, and its strengths and weaknesses. Additional discussion concerning other technologies not listed is contained in the Appendix (under Meeting Notes).

RECOMMENDATIONS OF THE EXPERT PANEL

The expert panel agreed that the following areas deserve priority for further research. These are listed below:

CW Defensive Systems (Breathable Air)

- The panel agreed that future research in this area should begin with basic fundamentals in order to determine the optimum long-term solution.

- The corona discharge process and the ceramic membrane process were proposed as good potential candidates for initial research.

- Liquid scrubbing with a reactive component (i.e., K-PEG process) may have application; however, the Navy is concerned with high humidity in the breathable air.

CFC Destruction (Non-Breathable Air)

- A literature search should be performed to assemble all available data on previous experience with conventional thermal oxidation (incineration) of CFCs.

TABLE 4. SUMMARY OF EXPERT PANEL RECOMMENDATIONS FOR NON-BREATHABLE AIR CASE

Process Name	Description	Phase	Status	Expressed Advantages	Potential Limitations
NON-BREATHABLE AIR (e.g., CFC Destruction)					
Catalytic Thermal Destruction	Destruction of organics at moderate temperature over a catalyst bed	G,L	C	Potential for thermal destruction at much lower temperature, resulting in better economics	Uncertainty regarding catalyst resistance to poisoning & attack
Chemical Scrubbing/ Destruction	Highly alkaline, non-aqueous scrubbing liquor	G	B	Superior to scrubbing alone, since equilibrium limitation is removed	May require pretreatment of feed to remove moisture
Conventional Thermal Oxidation (Incineration)	Incineration in direct flame	G,L,S	C	Reliable technology, proven track record with other hazardous wastes	Possible difficulty in selecting materials of construction resistant to corrosive attack; little actual data on destruction efficiency and PICs
Corona Discharge	High voltage generates excited electrons which dissociate hazardous wastes	G	B	Destruction occurs at ambient temperatures, rapid process	Requires high voltage power supply
Metals Scrubbing	Active metals such as zinc or aluminum	G,L	B,P	Rapid reaction forms salts (e.g., NaCl) which are easily removed	Uncertain ability to maintain active metal surface; may require pretreatment of feed to remove moisture
Pyrolysis	Thermal treatment in the absence of air	G,L,S	C	Smaller gas flow allows smaller downstream treatment equipment	May form larger amounts of PICs; possible difficulty in selecting materials of construction resistant to corrosive attack
Supercritical Water Oxidation	Treatment with water at supercritical conditions	L	B	Potentially higher destruction efficiency than Wet Air Oxidation	Greater energy requirements; not proven with CFCs; possible metallurgy limitations; aqueous streams only
Wet Air Oxidation	Treatment with water at moderate temperature	L	C	Process operated at moderate temperatures	Possible limitation to dilute streams only; aqueous streams only

G = Gaseous, L = Liquid, S = Solid, B = Bench-scale, P = prototype, C = Commercial

- Products of incomplete destruction (PICs) should be identified for residual ozone depletion potential and toxicity. In particular, the formation of F and Br analogs of dioxin should be investigated. Also, the thermal stability of CFCs and their basic combustion properties should be studied.

- Inorganic membranes should be studied from a materials science perspective. Also, new adsorbents should be investigated.

- The chemistry of scrubbing systems which contain a reactive component (i.e., K-PEG process) should be studied.

- The corona discharge process as it currently exists requires small scale tests, energy efficiency measurements, and modeling.

- Refractory linings that are resistant to HF should be studied and tested.

- Potential catalytic materials for catalytic thermal destruction should be evaluated.

SECTION 3

SPECIFIC RESEARCH TASKS TO ADDRESS RECOMMENDATIONS

The following is a more specific list of possible research activities to address the expert panel's recommendations.

For the breathable air case, the following research areas are proposed (listed in alphabetical order of the process):

Ceramic Membranes:

1. Study methods to produce materials with the smallest pore sizes to allow gas separations;

2. Investigate possible catalytic reactions and use of membranes as a catalyst support; and

3. Determine how large a pressure drop is required to obtain a good separation.

Chemical Scrubbing:

1. Determine effect of high humidity air on anhydrous scrubbing liquor;

2. Investigate various alkaline alcoholic agents and solvents (KOH, NaOH); and

3. Measure destruction and removal efficiency, solubilities of agents in oils, and vapor pressures of oils. Equilibrium data for agent in various oils will determine destruction and removal efficiency.

Corona Discharge:

1. Measure power consumption as a function of destruction efficiency;

2. Establish scaling rules and ability to model corona field; and

3. Investigate properties of ionized bed and reactive pellets.

Metals Scrubbing:

1. Investigate methods to retain active metal surface in the presence of air or water; and

2. Conduct literature search on Grignard reagents (i.e., zinc and aluminum).

New Adsorbents:

1. Characterize new materials; and

2. Measure adsorption isotherms with different compounds to determine uptake.

For the non-breathable air situation, the following research areas are proposed (listed in alphabetical order of the process):

Catalytic Thermal Destruction:

1. Conduct laboratory tests using simple plug flow reactor to evaluate catalytic materials in terms of activity and stability.

Chemical Scrubbing:

1. See previous discussion for breathable air case; and

2. Determine if CFCs are amenable to treatment with KOH, since preliminary literature review indicates that this is only effective in dehydrohalogenation (i.e., a neighboring hydrogen atom is required).

Corona Discharge:

1. See previous discussion for breathable air case.

Metals Scrubbing:

1. See previous discussion for breathable air case.

Pyrolysis and Conventional Thermal Oxidation (Incineration):

1. Perform a detailed literature review for data on thermal stability or combustion properties of CFCs.

2. Perform comparative evaluation of these technologies on the following factors:

   -- Thermodynamic calculations and modeling.

   -- Bench scale testing to obtain experimental data on PICs (using gas chromatography/mass selective detector (GC/MSD)).

   -- Based on the species identified in the bench scale testing, compare the toxicity and residual ozone depletion potential of the PICs from pyrolysis versus thermal oxidation.

3. Evaluate materials of construction suitable for use in this service such as:

   -- Refractory development program (to resist high temperature fluoride attack).
   -- Tail gas clean-up section for acid gases (HF,HCl).

Supercritical Water Oxidation and Wet Air Oxidation:

1. Measure destruction and removal efficiency as a function of temperature and oxygen concentration; and

2. Conduct literature search to determine what results (if any) have been obtained in other laboratories.

SECTION 4

CONCLUSIONS

The expert panel discussions on the most favorable technologies that warrant future development for CFC destruction and naval CW defense lead to the following conclusions:

1. There do not appear to be any new near-term technologies which are as capable as activated carbon in removing a broad spectrum of toxic CW agents from air onboard a Navy ship;

2. Longer-term options such as the corona discharge process and the ceramic membrane process should be pursued as research projects, where these options could lead to improved technologies for shipboard CW defense compared to conventional carbon adsorbers;

3. Thermal incineration appears to be feasible in the near-term for the destruction of bulk quantities of CFCs (such as contaminated refrigerants or waste solvents) although materials of construction for the incinerator and byproducts of combustion should be further researched; and

4. Sources of dilute emissions of CFCs may require technologies available in the longer-term. These options, which include technologies such as catalytic thermal destruction, pyrolysis, or wet air oxidation, may be source-specific.

APPENDIX A

MEETING NOTES (OPENING STATEMENTS AND DISCUSSION)

OPENING STATEMENTS BY PANEL MEMBERS

Mr. Dale Harmon, U.S. EPA/AEERL

Mr. Harmon discussed the work of AEERL in areas of global climate and stratospheric ozone. He mentioned the projects on second generation chlorofluorocarbon (CFC) substitutes and the current program to determine the recycleability of used refrigerant from auto air conditioners. He explained the overlap in Navy's interests regarding generation of breathable air from a emission control device.

Mr. Roger Gibbs, U.S. Navy/NSWC

Mr. Gibbs discussed his agency's role in developing chemical warfare defenses. In general, Mr. Gibbs is concerned with protecting ships under chemical warfare at sea. He described the physical properties of potential chemical warfare agents (see Table A1). Currently, the Navy uses activated carbon beds with impregnants added to react with the high volatility hazardous compounds that are not adsorbed on carbon, such as HCN. They currently use a cartridge that combines a fixed bed carbon adsorber and a HEPA (High Efficiency Particulate) filter. CFCs are also not strongly held on carbon, so this was one tie-in with CFC destruction technology. The Navy will consider high risk, high payoff technologies. They are interested in corona discharge and catalytic destruction. The ultimate goal is to eliminate problems with the carbon beds that include:

- Poor removal of highly volatile compounds such as hydrogen cyanide or cyanogen chloride;
- Requirement for periodic replacement;

TABLE A1. PHYSICAL PROPERTIES OF CHEMICAL WARFARE AGENTS

Parameter	Low	High
Molecular Weight	30	364
Volatility (mg/m^3)	11.22	1.28×10^{12}
Vapor Pressure (mmHg)	7.8×10^{-4}	7.97×10^{8}
Boiling Point (°C)	-151	298
Lethality (mg/m^3-min)	10	15,000

- The need for a regenerable system due to logistical problems; and

- Lack of specificity, e.g., the carbon beds will adsorb other compounds such as water vapor, jet fuel vapors, and missile exhaust, thus lowering the available capacity.

Gas masks are used for individual protection.

Don Oberacker (EPA/HWERL) asked about coordination with the Army, especially regarding destruction of obsolete munitions: Mr. Gibbs responded saying that the Army is the lead agency for CW and destruction of obsolete munitions is the Army's program. He said that the Navy and the Army are required to coordinate, and that the Navy budget is less than 1/10th of what the Army budgets for CW.

Jose Bravo (UT/Separations Research Lab) asked about absorption of CW agents into paints and other surface coatings. Mr. Gibbs responded by discussing the Navy's work in the area of strippable coatings.

Dr. Barry Dellinger (Univ. of Dayton/Incineration Research)

Dr. Dellinger spoke from his prepared papers. He discussed the differences in predicted products of destruction between equilibrium calculations and kinetics. He stated that it would be better to produce HCl rather than Cl_2 because HCl is much easier to scrub out. The formation of HCl or Cl_2 would depend on the relative abundance of H and Cl; or more generically, H and X, where X is a halogen. Dr. Dellinger also explained the influence of the "Deacon reaction" which involves $2HX + 1/2\ O_2 \rightarrow H_2O + X_2$. For the case of F and Cl, this reaction would promote the formation of HF and Cl_2. He described the flame inhibition problem attributable to halides. Scavenging by halides results in a reduction of free OH radicals, which are considered the chain carriers in combustion reactions. He stressed that incineration is a function

of time; real situations cannot be modeled using equilibrium calculations. His measurements on CFCs have been hampered by poor detector response to fluorine (doesn't show up well on FID). He showed a model for destruction of fully-halogenated CFCs (11, 12, 113, etc.) as the initiation being bond homolysis, which is the rupture of the carbon-halide bond. He presented some data for destruction temperatures of various CFCs.

On the subject of products of incomplete combustion ("PICs"), Don Oberacker asked if brominated compounds (e.g., halons) would produce more toxic products than fluorine. In either case, he wondered about the formation of Dioxin-analogs (F or Br instead of Cl). Dr. Dellinger explained that it is very likely that PICs may be higher molecular weight compounds compared to the parent (starting) materials. Garry Howell (EPA/HWERL) stated that one of the reasons that CCl_4 fire extinguishers were banned was due to the formation of phosgene (COCl). Ron Bell (Radian) asked if the stoichiometry was sub-stoichiometric as this would affect the PIC/POCH (Principal Organic Hazardous Constituent) ratio. Dellinger stated that these were sub-stoichiometric due to real-life mixing problems in commercial incinerators.

Mr. Jose Bravo (Univ. of Texas/Separations Research)

Mr. Bravo spoke about three (3) primary areas for possible application:

- Tailor-made or specialty adsorbents; these would include zeolites, other crystalline aluminas, or possibly ion exchange resins.

- Membrane separations; he was not optimistic about the use of polymeric membranes, but mentioned new developments in the areas of inorganic membranes. These could include ceramic materials (aluminas again), or carbon molecular sieve type. He explained that these could be used as catalyst supports.

- Absorption; he proposed scrubbing processes in conjunction with chemical reaction.

In another general comment, he emphasized that separations in combination with chemical reaction was a definite advantage. This type of process would benefit from the fact that equilibrium limitations would be removed if the compound of interest could be simultaneously captured and destroyed.

Mr. Don Matter (Rollins Environmental Services/Incineration)

Mr. Matter explained that Rollins has incinerated waste CFCs since 1969. Their incinerators can achieve high destruction and removal efficiencies (DREs) of 99.99 to 99.9999%. He cited the example of a test burn in their New Jersey incinerator with CFC-22 that achieved 99.9994% DRE. The temperature is over 2000°F with between 2.3 to 2.5 seconds average residence time. The temperature in the flame front may be as high as 2600°F to 3200°F. Rollins operates several slagging rotary kilns. He discussed the problems of incinerating CFCs in terms of the potential for severe scrubber corrosion. The scrubber section has a drastic temperature change from around 2200°F to 185°F in a short duct. Also he talked about the problems within the incinerator, particularly the refractory lining. They have painstakingly worked to develop a resistant refractory lining for their New Jersey incinerator. They currently restrict CFCs to less than 5% of the waste burned in the New Jersey incinerator and less than 100-200 ppm in the Baton Rouge, LA and Texas incinerators. He described the types of CFC wastes that they have destroyed:

- Still bottoms from CFC production which contain 5 ppm fluorocarbons;
- One ton cylinders of refrigerant; and
- Cases of aerosol cans.

He described their tail gas treatment process: they have plenty of excess H_2, so there is no problem with formation of Cl_2 or F_2. Their scrubber sludge is noticeably heavier when they incinerate CFCs; it contains $CaCl_2$. Disposal costs for the kiln ash and scrubber sludge are approximately $165 per ton.

Mr. Don Oberacker (U.S.EPA-HWERL/Thermal Treatment)

Mr. Oberacker reviewed the history of EPA's experiences with incineration of hazardous wastes. He also discussed what he felt were the primary needs for additional information regarding CFC destruction. These needs included the following:

- More bench scale testing to determine temperatures of destruction, products formed in the destruction process (breakdown products or PICs), and possible formation of fluorinated dioxin analogs.

- Pilot and/or full scale testing with such technologies as the rotary kiln or liquid injection incinerators. This might be done at an EPA lab such as the Combustion Research Laboratory in Arkansas.

He also mentioned the experience with combustion of aluminum pot liner waste; these wastes contain fluorine, and the offgas contained F_2. He mentioned that in the destruction of ethylene dibromide (EDB), the bromine was controlled by adding sulfur to form HBr, which could be scrubbed out.

Mr. Matter (Rollins) stated that DuPont knows all about CFC destruction, but needs the appropriate forum to present such information.

Mr. Garry Howell (U.S.EPA-HWERL/Chemical Treatment)

Mr. Howell discussed his background with destruction of EDB using the K-PEG process, which uses potassium hydroxide (KOH) in polyethylene glycol (PEG). This process has been used to destroy PCBs. The PEG serves as a phase transfer catalyst (to improve solubility in the oil phase). His other suggestions included:

- Zinc (or other active metals) which serve as Grignard reagents to dehalogenate the compound. He described the reaction between zinc and trichloroethylene (TCE) as "explosive"; and

- A patented process using a low temperature eutectic mixture of molten salts. This process uses $NaNO_3$, NaOH, and Na_2CO_3 to react with the halocarbon. The $NaNO_3$/NaOH ratio should be controlled so that NaCl will precipitate out of solution.

To combat the corrosion problem in incinerators, he recommended zirconia (Zr_2O_3) refractory. He said that this material is used in oxygen detectors for combustion processes (incinerators).

Dr. Norm Plaks (U.S.EPA-AEERL/Corona Destruction)

Dr. Plaks talked about the development work underway at AEERL on a corona destruction process. This process uses high voltages of AC or DC current to generate an ionized corona discharge. The energized electrons are capable of dissociating the compounds of interest. In order to obtain high DREs, several stages are connected in series. He discussed modifications to the basic design such as a fixed bed of high resistance pellets, or a non-conductive layer. These alternatives may offer the possibility of performing both a destruction and neutralization process simultaneously.

Mr. Joe McSorley (U.S.EPA-AEERL/Combustion Research)

Mr. McSorley talked about the various programs underway in the area of combust3ion research. Some of the projects mentioned included:

- Tunnel Furnace used to perform droplet studies;
- Rotary Kiln used to study the effects of containerized waste destruction;
- Package Boiler Simulator used to test a low-NOx burner; and
- Circulating Bed Combustor (developed by Ogden Environmental).

Mr. Ron Bell (Radian Corp./Incineration)

Mr. Bell talked about his experiences in incinerator design and start-up. He mentioned problems with the refractory lining. The point of waste injection is the coolest spot in the combustion zone and is subject to thermal stresses. Downstream problems are corrosion related. He stressed the need to maintain the flue gas above the acid dewpoint to prevent condensation and resulting corrosive attack. He pointed out that high excess air (typically used to obtain complete combustion of the waste or fuel) also results in the potential formation of Cl_2 (instead of the preferred form, HCl). He described the problems which may occur from acid mists. These submicron-sized aerosols may be formed upon quenching, and are most difficult to remove. Special treatment such as "Brinks" mist eliminators or venturi scrubbers might be required.

Dr. Frank Castaldi (Radian Corp./Biological Treatment)

Dr. Castaldi talked about problems with applying biological processes to destruction of "refractory" compounds such as CFCs. Since there are no natural compounds with structures similar to CFCs, naturally occuring organisms have not developed which could utilize CFCs as a nutrient. Thus, he felt that organisms which could break down CFCs would have to be genetically modified for this purpose. He stated that CW agents would be more susceptible to biological treatment than CFCs. Biological treatment is limited to the ppm/ppb range only, and is most commonly used on aqueous streams or soil. Another general limitation is the relatively long time frame for degradation.

Dr. David DeBerry (Radian Corp./Chemical Treatment)

Dr. DeBerry discussed several types of chemical processes:

- Hydroxy ($^{\cdot}OH$) radical attack. This process was not expected to be successful for CFC destruction, but might be effective at destroying CW agents;

- Active metals. He described the use of active metals such as sodium, potassium, aluminum, or zinc to destroy CFCs. Wastes that contain water and oxygen may pose problems;

- Wet air oxidation is a process which uses a moderately high temperature (>300°C) aqueous stream with oxygen to destroy organic compounds. This process may not be effective for CFCs due to their resistance to oxidation, but might be successful based on hydrolysis.

Dr. DeBerry also discussed the corrosion problems which might be caused by CFC destruction. The fluorides and chlorides liberated from CFCs would require

the use of special materials of contruction. Specifically, he noted that although titanium materials are resistant to Cl, they are attacked by F.

VENDOR PRESENTATIONS

Dr. Hugh Reilly (Sandia National Laboratory/Solar Destruction)

Dr. Reilly (and two other scientists from Sandia) spoke about their solar furnace development program. Their unit has been tested as a methane reformer, but they proposed a modification to serve as a thermal destruction device for CFCs. Many unknowns were identified, such as the relative contributions of thermal, catalytic, and photolytic destruction.

Dr. Larry Britton (Texas Research Institute/Biological Treatment)

Dr. Britton presented material on the biological treatment of man-made organic compounds. He stated that halogenated compounds are more resistant to biological degradation than similar alkanes or alkenes. He explained that halocarbons can be degraded by aerobic or anaerobic conditions. The organisms degrade these compounds through a "cometabolic transformation". In other words, the organisms still require a primary nutrient source, but are also tolerant of the halogenated compounds. The carbon is oxidized to CO_2, and the halogens are converted to their respective salts (e.g., KCl or NaCl in the case of chlorine). Chemical warfare agents may be more susceptible to biological treatment than halocarbons; he cited experience with enzymatic hydrolysis of organophosphorous compounds.

DISCUSSION

1. CW Defensive Systems for Breathable Air

Mr. Gibbs began by elaborating on their needs for improved CW defensive systems. The Navy needs a constant air purification system that is

not affected by H_2O. Incineration is too energy intensive. Carbon does not adsorb HCN and CNCl well, and is also "blinded" (its capacity is reduced) by H_2O. Specific impregnants (silver, copper, and chromium salts) are needed to react with the HCN/CNCl. However, the impregnants reduce the capacity of the carbon, are non-selective, and therefore cause difficulty in knowing when the impregnated carbon needs to be replaced. He stated that the Navy would prefer a "passive" system; it would be more reliable and require less attention. The Navy will probably continue to use carbon, but would like to have a device installed upstream (such as corona destruction or oil scrubbing). He did not find staged adsorption to be an attractive option. He was also interested in continuous pressure swing adsorbtion (PSA) using carbon molecular sieves.

One suggestion proposed for the Navy was routing the contaminated air through the onboard gas turbines or boilers to destroy the CW agents. Catalysts and pre-heat were also proposed in conjunction with this idea; Mr. Gibbs said that this type of option would require economic evaluation.

Mr. Bravo was asked to elaborate on the concepts using inorganic membranes or tailor-made adsorbents. He explained that commercial processes exist that purify water using either carbon molecular sieves or ceramic membranes. He felt that the emphasis for development should be on the materials science aspects and not on process engineering. Inorganic membranes need improved strength and durability. He discussed the advantages of the MSC (molecular sieve carbon) over ordinary activated carbon. The MSC (under development in Israel) has a well-defined pore size distribution, resulting from the fact that it is produced by pyrolysing a synthetic organic polymer structure. Only the carbon "skeleton" remains. This offers the advantage of more controlled and consistent properties compared to coconut-based activated carbon, for instance. The MSC can be fabricated as a hollow fiber, a cast sheet, or in pellet or granular form. In general, membranes work best to concentrate dilute streams. It is more desirable to pass only the small mass of contaminant through the membrane than to pass the entire bulk flow. In

contrast to adsorption systems, the "capacity" of a membrane is very low, it functions through separation, not retention.

Mr. Bravo also spoke on the subject of new adsorbents (such as zeolites and aluminas). He cited a recent issue of Chemical Engineering Progress (February 1988) which was devoted to zeolites.

On the subject of scrubbing processes for CW defensive systems (such as the K-PEG process), several points were raised. First, the choice of scrubbing liquid was discussed. The consensus seemed to be that a highly refined oil with a low vapor pressure would be desirable. Possible candidates include the silicone or fluorocarbon oils, which may be nonflammable as well. It was not clear how water would be prevented from entering the scrubber with the contaminated air, but the alkaline component of this process would not tolerate much water. Also, it was considered important to prevent entrained scrubbing liquid from contaminating the downstream carbon bed. Mr. Howell felt that development of the process for the Navy's application could be a good research project.

2. CFC Destruction

Mr. Matter was asked again about the types of CFC-containing wastes that Rollins incinerates. He said that they regularly dispose of by-products from CFC production processes, still-bottoms which contain residual CFCs (1,000 to 2,000 gallons per month), waste solvents containing CFCs, and less frequently, aerosol cans or off-spec refrigerant in large one-ton cylinders. He repeated that Rollins uses a specialized refractory brick and mortar in the kiln throat where the temperature difference is greatest. Mr. Matter also stated that public data already exists on the subject of PICs from CFC-containing waste incinerators in the RCRA Part B Test Burn Permits.

The possibility was raised of destroying certain CFC emissions (from solvent cleaning or foam blowing, for example) in existing on-site equipment

such as furnaces or boilers. Mr. Bell discussed some potential problems with sending CFC-laden gases to on-site boilers:

- If a superheater is used, the tubes in this area may be hot enough to be attacked directly by acid gases; and

- If an economizer is used, it is possible to cool the flue gases to the acid dew point, resulting in condensation and localized corrosion. Mr. Matter added that it is common practice in Europe to send halocarbons to an available waste heat boiler.

Dr. Dellinger emphasized that PICs from CFC destruction may consist of olefinic halocarbons. These compounds would have to be tested for toxicity and possible residual ozone depletion potential. He also stated that combustion was not necessary to destroy CFCs, since they are thermally decomposed. A pyrolysis process might be smaller and cheaper.

There was a discussion regarding the other types of destruction processes. Dr. Smith (U.S.EPA/AEERL) mentioned that PIMA (insulation foam manufacturers trade association) was interested in the possibility of landfilling old CFC-containing foam. Dr. Castaldi felt that this was not promising from a biological degradation perspective because of the time scale. The question arose: "why bother to landfill if you can just incinerate?"

Mr. Howell was asked about his experience with a wet oxidation process using sodium salts. He stated that acetic acid had been destroyed by the $NaNO_3$/NaOH mixture, and that a surface catalytic effect with Hastelloy C was noted. The tests were conducted in an autoclave at 300°C.

Photolysis was proposed as a destruction technology, since this is the mechanism by which CFCs are decomposed in the upper atmosphere. It seems that this process is too slow compared to more conventional processes. The "LARK" process (which used Hg or Xe arc lamps to generate high intensity

light) was mentioned, but the experiments showed a slow photolysis rate. Dr. Dellinger felt that photolysis may be enhanced at elevated temperatures.

Regarding the plasma arc processes (for example, Westinghouse Plasma Systems), Mr. Oberacker cited unfavorable test results showing formation of PICs in larger than expected amounts. He felt that it would likely require a downstream afterburner and cleanup systems as well. Thus, the plasma system begins to look more like a conventional incinerator. Mr. Oberacker also described his experience with a microwave plasma destruction process. He felt that the costs were high, and successful operation was "more art than science."

APPENDIX B

HANDOUTS FROM EXPERT PANEL AND VENDOR PRESENTATIONS

Mr. Jose Bravo, Separations Consultant, University of Texas

ROLE OF SEPARATIONS TECHNOLOGIES IN THE COLLECTION AND DESTRUCTION OF CFCs AND HALONS

Separations technologies will play an important role in the collection and destruction of halocarbons at two different levels; separation of the halocarbons themselves from carrier streams for the purposes of decontamination and purification, and the removal of potentially harmful by-products generated during destruction of the halocarbons. The role of separations in the purification of halocarbons for reuse and recycle will be of lesser importance in the future; furthermore, the applicable technological concepts (mainly distillation) used for this are very similar to those applied in the manufacture of the halocarbons and thus is fairly well known and widespread.

The problem of dealing with gaseous or liquid streams that contain small amounts of halogenated pollutants, particularly CFCs, poses an important technological challenge in the field of separations. The techniques of choice should be ones that tend to concentrate and immobilize the contaminants for easy disposal.

Adsorption onto a solid from either a gaseous or a liquid stream can undoubtedly perform the necessary removal from the carrier stream provided the adsorbent is selected carefully or even tailor made. Adsorption is the technique that offers the best possibility at this time of producing essentially pure carrier stream. This can be of great importance in military decontamination applications where breathable air is to be obtained from contaminated environments.

The technology for manufacturing high-performance, specialty adsorbents is growing by leaps and bounds. The limiting factor in the applicability of adsorptive processes for the removal of halocarbons continues to be the regeneration step. The design of the adsorbent can play a major role in the ease of regeneration and on the overall applicability of the process. An excellent combination could be to achieve the regeneration of the adsorbent with a gaseous fuel so that the pollutant is destroyed when the fuel is burned.

Membrane technology can also find wide application for the removal of halogenated organics from air and water. Membrane selectivity will be the largest barrier that needs to be overcome and the way to do this is by a materials science approach. The limiting factor in the application of membrane technology in the fields where potential exists is in the material science and not in the process engineering aspects. Combinations of membrane technology with others, such as stripping and adsorption, can prove to be the most cost-effective schemes, because the selectivity limitation can be dealt with through recycle.

New membrane materials, such as carbon molecular sieves and ceramics, can prove very useful in cases where mechanical and chemical resistance are imperative. These sturdy materials offer the possibility of effecting a destruction reaction in conjunction with a membrane separation to favor the thermodynamics of total destruction. One could even envision a catalytic membrane that would enhance the rate of reaction and at the same time remove the products of reaction as they are formed, thus reducing the effect of equilibrium limitations.

Extraction techniques, in particular, high pressure or supercritical extraction (SCFE), offer the potential for easy recovery of concentrated halocarbons from dilute water feed streams. Co-solvent technology can have a great impact on the ability of SCFE to find industrial implementation in the removal of CFCs from water.

Still another interesting possibility is that offered by a combination of absorption and chemical reaction where the pollutant could be removed from a gaseous stream into an absorbing liquid. Once in the liquid phase, a chemical reaction, such as a hydrolysis, could render the pollutant harmless and make it easy to dispose of. Alternatively, the pollutant could be absorbed into a liquid fuel stream to be sent to a combustion chamber designed to effectively incinerate the pollutant as the fuel is burned for energy.

Air and steam stripping are proven, cheap methods for dealing with volatile halocarbons. Combinations of air stripping and gas phase adsorption have proven to be very effective for the removal of some chlorinated hydrocarbons from source and supply waters. This could also be the case for dilute streams of CFCs in water. The interesting research issues in the areas of air and steam stripping deal with the development of more effective mass transfer devices.

The complete destruction of CFCs and Halons will produce, in the best of cases, some environmentally harmful compounds such as hydrogen halides and halogen oxides. These can be effectively dealt by absorption, followed by neutralization with a strong sodium or potassium base rendering the halogens harmless.

United States Patent [19]

Howell et al.

[11] **Patent Number: 4,497,782**

[45] **Date of Patent: Feb. 5, 1985**

[54] **METHOD FOR DESTROYING TOXIC ORGANIC CHEMICAL PRODUCTS**

[75] Inventors: **Samuel G. Howell**, 4660 Aston Dr., Cincinnati, Ohio 45244; **William R. Birchall**, 55596 Country Club Rd., South Bend, Ind. 46619

[73] Assignees: **S. Garry Howell**; **Lloyd Watson**, both of Cincinnati, Ohio; **William R. Birchall**, South Bend, Ind.; **Larry Allen**, Ft. Mitchell, Ky.

[21] Appl. No.: **570,853**

[22] Filed: **Jan. 16, 1984**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 437,434, Oct. 28, 1982.

[51] **Int. Cl.**[3] **C01D 3/00**

[52] **U.S. Cl.** **423/184**; 423/659; 423/DIG. 12; 55/228

[58] **Field of Search** 423/DIG. 12, 184, 659; 55/228

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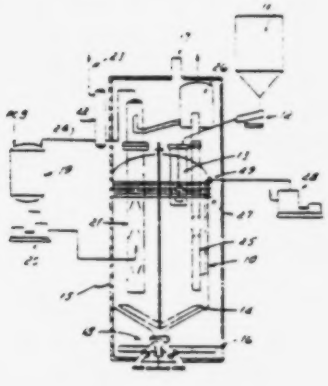
Primary Examiner—John Doll
Assistant Examiner—Robert L. Stoll
Attorney, Agent, or Firm—Wood, Herron & Evans

[57] **ABSTRACT**

A method for destroying toxic organic chemical products. The method is particularly adapted for the destruction of polyhalogenated polyphenyls, especially polychlorinated biphenyls (PCBs). The toxic organic chemical product is intimately contacted and reacted with a molten mixture of an alkali metal hydroxide and an alkali metal nitrate, so that it is converted to harmless products which, in the case of PCBs, include a halide salt, at least one carbon oxide, and water. By incorporating a substantial excess of nitrate in the mixture most of the salt is caused to precipitate and to settle out to the bottom for easy removal.

15 Claims, 2 Drawing Figures



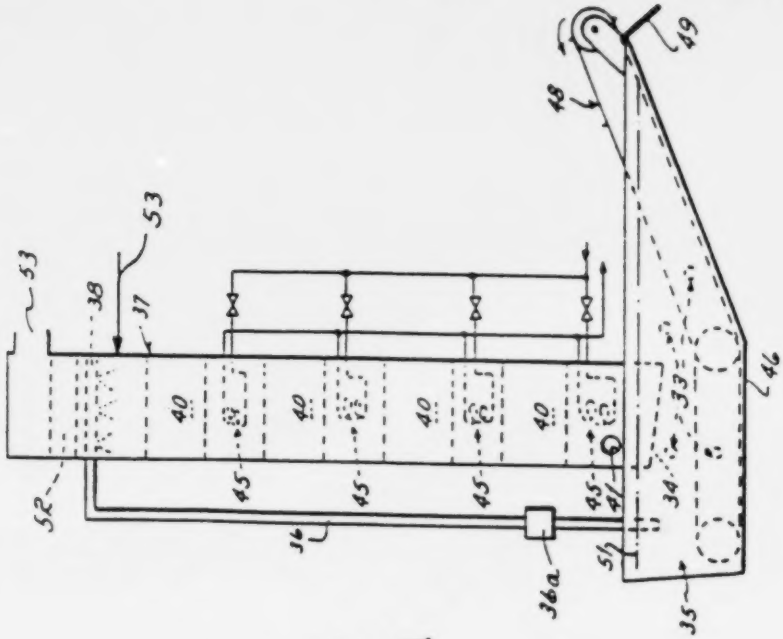

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FIG. 2

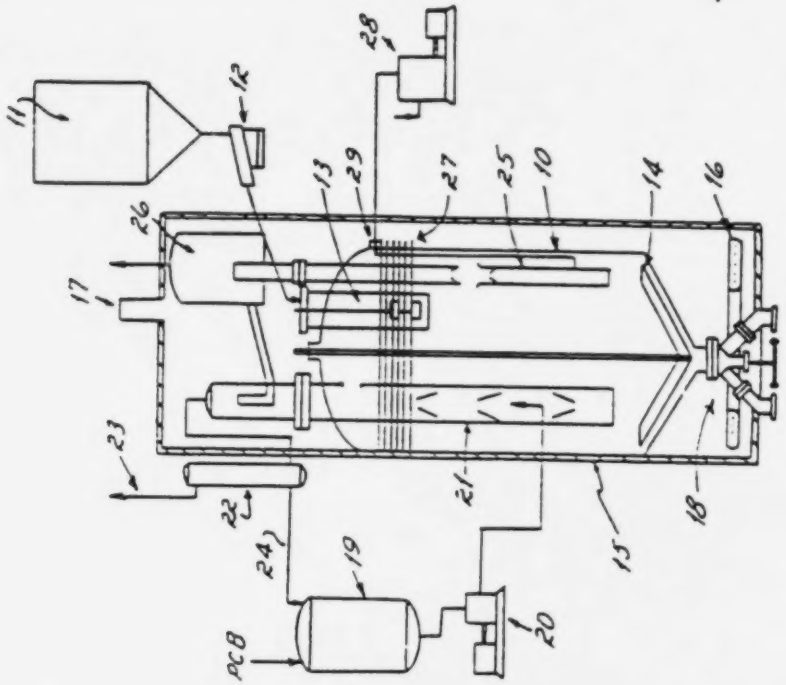
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FIG. 1

METHOD FOR DESTROYING TOXIC ORGANIC CHEMICAL PRODUCTS

RELATED APPLICATION

This application is a continuation-in-part of our co-pending U.S. patent application Ser. No. 437,434, filed Oct. 28, 1982.

FIELD OF THE INVENTION

The present invention relates to a method for destroying environment-contaminating toxic organic chemical products, including polychlorinated biphenyls.

DESCRIPTION OF THE PRIOR ART

The problem of environmental contamination caused by toxic materials and the related health risks to all forms of life has become of major concern as industrial societies seem to create ever increasing numbers of toxic chemical products, particularly organic products. Environmental contamination may occur by reason of the toxicity of such a product, per se, or by reason of the toxicity of by-products formed during the use of such a product, or by reason of the toxicity of by-products formed during the manufacture of such a product. The problem of environmental contamination has become of such magnitude, in fact, that the federal government and many state governments have established independent agencies charged with the responsibility of controlling, or at least minimizing, all forms of environmental contamination.

Environmental contamination occurs in a number of ways. It may, for instance, occur when toxic products resulting from the combustion of petroleum, coal and other carbonaceous energy sources are released directly into the atmosphere, as during the operation of vehicular engines. Such contamination also occurs at industrial installations that rely on carbonaceous fuels as energy sources. At least in the United States, vehicular gasoline engine emissions are now required by law to be catalytically oxidized to less obnoxious by-products prior to being discharged to the atmosphere. Emissions from coal and other carbonaceous fuel-burning industrial installations are similarly treated, or are burned at very high temperatures in afterburners. Various other means and methods have been proposed to treat environment contaminating emissions of this type. One such proposal is discussed in Greenberg U.S. Pat. No. 3,647,358 and involves subjecting industrially generated carbon and hydrocarbon waste products to the catalytic action of a molten salt bath at temperatures below the normal combustion temperatures of such waste products, without chemical reaction occurring between the waste products and any of the components of the salt bath.

Environmental contamination also occurs when toxic organic chemical products that are not the products of combustion of carbonaceous fuels, enter the environment. Such toxic organic chemical products may be primary products, i.e., those manufactured for a specific use such as, for example, a herbicide, pesticide, insecticide, or the like. They may be secondary products, i.e., by-products resulting from the manufacture of primary products. Toxic organic chemical products may enter the environment in various ways, for example, by release to the atmosphere during their manufacture, or by release into water supplies by leaching from agricultural lands to which they have been applied or from landfills into which they have been deposited without detoxification, or by release from other products in which they have been used as components.

The toxic organic chemical products above referred to often take the form of polynuclear aromatic organic compounds which are substituted on the nucleus by halogen, sulfur, or phosphorous atoms. Representative of this type of toxic organic chemical products and those to which the method of this invention is particularly directed, are polyhalogenated polyphenyl compounds and, more particularly, polychlorinated biphenyls, often referred to simply as PCBs. PCBs, and polyhalogenated polyphenyls in general, are prepared by the direct chlorination of the selected polyphenyl compound which results in a mixture of isomers the bulk of which, in the case of PCBs, are reported to be the trichloro- and tetrachloroisomers, with the balance being the other isomers. The polychlorinated polyphenyls, including the PCBs, are considered to have excellent properties of inertness, fire resistance and thermal stability, all of which has rendered them highly suited for use in a variety of areas including varnishes and paints, copy paper, plasticizers, printing inks, lubricants, and particularly in electrical transformers and capacitors.

Although PCBs have been known chemically for many years and have been manufactured and used commercially for quite some time in the several areas noted above, the significance of their toxicity has only been recognized more recently. Because of this lack of knowledge concerning their toxicity, these products were permitted to enter the environment through uncontrolled burning and direct disposal into public sewage systems and landfills without regard to the possible consequences of these acts. The seriousness of this earlier uncontrolled disposal of PCBs, and related toxic products, is now recognized in the light of more recent knowledge that these products are very resistant to biodegradation and will, accordingly, persist in the environment for long periods of time.

The conventional way to destroy toxic organic chemical compounds has been to subject them to burning at very high temperatures, as above described with respect to the products of combustion of carbonaceous fuels. PCBs, however, are known to be quite resistant to oxidation, so that when these, and related products, are subjected to burning in conventional industrial furnaces, it often is impossible to maintain the high destructive temperatures for the required residency time necessary to convert them to carbon dioxide, water and hydrogen halide. In order to attain these high destructive temperatures, i.e., greater than 1100° C., and to maintain them for a residence time sufficient to totally destroy the PCBs, therefore, requires specialized furnace equipment which can be costly to fabricate. Moreover, since aromatic halogen derivatives such as PCBs have notoriously low fuel values, destruction of such products by burning necessarily requires an external heat source in order to reach and maintain the conversion temperature. Finally, destruction of PCBs and related halogenated products produces highly corrosive hydrogen halide acids which should be neutralized before discharge, preferably at a point in the procedure designed to minimize their corrosive effect on the furnace and allied equipment.

Reference was earlier made herein to Greenberg U.S. Pat. No. 3,647,358 which suggest the use of a molten salt bath as a catalytic oxidizing medium for the destruc-

tion of various industrially generated carbon and hydrocarbon waste products. The use of a molten salt bath has also been proposed in U.S. Pat. No. 4,145,396 by treating waste materials containing a radioactive element. The use of a melt of a hydroxide by itself to decompose PCBs is taught in Japanese patent application Ser. No. 7196/73, filed Jan. 16, 1973. The use of a molten solvent has also been proposed in U.S. Pat. No. 3,845,190 for the disposal of certain types of organic pesticidal compounds. None of these, however, is concerned with the destruction reaction here involved, and none enables the solid reaction product to be so easily removed, which is an important advantage for continuous operation.

SUMMARY OF THE INVENTION

Notwithstanding the fact that PCBs are no longer commercially manufactured in the United States and are totally banned in some areas of the world, the environmental hazards of these products continue to exist simply because there are other areas of the world where PCBs continue to be manufactured and used, albeit under varying degrees of governmental control in most instances. Moreover, the most widely applied area of use for PCBs in the United States has been in electrical transformers and capacitors which have useful lives of many years, but which, on eventual replacement, must have their PCB content totally destroyed. Currently, the only procedures which have been accepted by the U.S. Environmental Protection Agency for destroying PCBs and related toxic halogenated products are destruction by burning, a procedure that has the several disadvantages noted above, and by treatment with sodium metal, an expensive treatment which is limited to dilute, nonaqueous solution of PCBs. Accordingly, there has remained a serious need for an improved method for destroying PCBs and related halogenated products.

It is a principal object of this invention to provide such a method. It is a further object of this invention to provide a method of destroying PCBs and other toxic organic chemical products that is total in its effect and in compliance with the standards established by the U.S. Environmental Protection Agency. A still further object of this invention is to provide a method for destroying PCBs and other toxic products that does not require the excessively high temperatures demanded by burning. It is also an object of this invention to provide a method of destroying PCBs and related halogenated products that does not result in highly corrosive, or otherwise objectionable, emissions. Another objective of this invention is to provide a method of destroying PCBs and related halogenated products that can also be used effectively to destroy other types of toxic organic chemical products such as, for instance, organic aromatic compounds substituted by sulfur and/or phosphorus atoms.

These various objects are met in accordance with this invention by providing a method of destruction that comprises reacting the toxic organic product with a molten mixture of an alkali metal hydroxide and an alkali metal nitrate to form an alkali metal salt, under conditions such that the salt is precipitated from the molten mixture and settles out. More particularly, in a specific embodiment the method of this invention comprises intimately mixing PCBs, or related halogenated products, with a molten alkali metal hydroxide-alkali metal nitrate mixture, under such conditions of temperature, time, and melt composition as will cause the total destruction of the PCBs by converting the halogen content to an alkali metal halide salt which is precipitated, and by converting the carbon and hydrogen content to carbon dioxide and water, which are released in vapor form.

While it is not the intention to restrict this invention by any particular theory of operation, it would appear that the method involves the reaction of the PCBs by the alkali metal hydroxide to form the corresponding alkali metal halide, one or more carbon oxides, and water. Notwithstanding the property of unusual inertness that PCBs are known to possess, it has, nevertheless, been reported in the literature that under very extreme conditions PCBs will react with sodium hydroxide to form a dehalogenated biphenyl as an organic secondary reaction product ("Chlorinated Biphenyls and Related Compounds" by R. E. Hatton, *Encyclopedia of Chemical Technology*, Kirk-Othmer, Wiley Interscience Publications, Wiley & Sons, 1st Ed., Vol. 5, pp. 844–848). The dehalogenated biphenyl resulting from the alkali metal hydroxide reduction is then apparently oxidized by the alkali metal nitrate, principally to water and carbon dioxide, the alkali metal nitrate being reduced in the latter reaction to the alkali metal nitrite. In further consideration of the theory of operation, practice of the method of the invention appears to have shown some apparent evidence of a synergistic effect of the two component molten bath, since a melt of either component alone fails to produce the same degree of destruction. In any event, whatever the theory, destruction of PCBs and related halogenated products by the method of this invention is complete in an environmental sense so as to comply with the standards established by the United States Environmental Production Agency for these products.

The proportion of nitrate and hydroxide should be sufficient to stoichiometrically react with the toxic feed. Beyond that, however, it has surprisingly been found desirable to maintain a substantial excess of nitrate over the stoichiometric proportion actually needed to oxidize the organic secondary reaction product, e.g., the dehalogenated biphenyls. It has been determined that use of a substantially higher proportion of nitrate than required for reaction reduces the solubility of the reaction product salt in the melt, and thereby facilitates precipitation of salt from the liquid phase. Moreover, it has further been found that increasing the proportion of nitrate reduces the viscosity of the mixture, thereby enabling the precipitated salt particles to settle out from the melt and to collect at the bottom. This greatly facilitates removal of salt from the reaction site, and is especially useful in a continuous or semi-continuous process.

The mol amount of nitrate to be used should be at least twice that of the hydroxide present. In respect to the salt, the amount of nitrate should be such as to cause the salt to exceed its solubility limit and so to precipitate. The optimum proportions depend on melt temperature, the nature and concentration of the salt, and other factors. For a given set of circumstances the optimum proportion can be determined by a series of comparative tests, in which the amounts of hydroxide and salt are held constant and the proportion of nitrate is gradually increased. An NO_3/OH mol ratio of about 3:1 is preferred where the nitrate is regenerated and reused, and where the OH/PCB ratio is near unity. At very high ratios of nitrate to hydroxide it appears that salt solubility begins to increase, so that above that level salt

is not so readily precipitated from the melt. At present, it appears that $NaNO_3/NaOH/PCB$ ratios of at least 2:1:1 will usually accomplish salt precipitation, and substantially higher ratios are preferred.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view illustrating a system for carrying out the method of this invention, wherein the toxic product is in liquid form;

FIG. 2 is a schematic view illustrating the presently preferred continuous method for the practice of the invention, wherein the toxic product is vaporized.

DETAILED DESCRIPTION

Referring now to FIG. 1, there is schematically represented an enclosed chemical reaction vessel 10 adapted to hold the hydroxide-nitrate molten bath in which the destruction of a toxic organic chemical product, such as PCBs, is to be carried out. Reference numeral 11 indicates a hydroxide-nitrate mix storage hopper from which the mix is fed by mix feeder 12 through mix feed column 13 into reaction vessel 10, wherein it is kept in an agitated condition by agitator blade 14. Surrounding reaction vessel 10 is a heating enclosure 15 provided with a heating element 16 by means of which the hydroxide-nitrate mix is maintained in a molten state. Provided at the top of heating enclosure 5 is an exhaust vent 17 for discharge of the heating element products of combustion, while at the bottom of heating enclosure 15 and associated with reaction vessel 10 is a salt discharge valve 18 through which alkali metal halide can be withdrawn. Reference numeral 19 indicates a toxic product storage tank from which the product intended for destruction is fed by means of pump 20 into reactor 10 through toxic product feed column 21, the lower end of which extends beneath the surface of the hydroxide-nitrate molten bath. The upper end of toxic product feed column 21 extends through the enclosed top of reaction vessel 10 into the upper section of heating enclosure 15 from which it communicates with reflux condenser 22 on the exterior of heating enclosure 15. Reflux condenser 22 is provided with exhaust means 23 for venting uncondensed reaction vapors from reaction vessel 10 to the atmosphere, and a condensate line 24 for refluxing condensed reaction vapors from reaction vessel 10 back to toxic product feed column 21. The upper end of a nitrite oxidizing column 25 extends through the enclosed top of reaction vessel 10 and communicates with a demister 26 in the upper section of heating enclosure 15, from which it communicates directly with reaction vessel 10 through toxic feed column 21 and indirectly therewith through reflux condenser 22. Surrounding reaction vessel 10 is a heat exchanger 27 for preheating air passing from air compressor 28 into nitrite oxidizing column 25 through air valve 29.

In carrying out the method of this invention using the apparatus of FIG. 1, the hydroxide-nitrate mix selected to constitute the melt is conveyed from hydroxide-nitrate storage tank 11 into reaction vessel 10 via feeder 12 and mixer 13. The metal-based components of the mix may be any member selected from the class of alkali metals but, for purposes of the method of this invention, the hydroxides and nitrates of sodium and potassium are preferred as a practical matter because of their common industrial availability. Whether or not the metal-based components of the hydroxide and nitrate are the same as or different than one another appears to be immaterial from the standpoint of the efficacy of the method but, as a practical matter, they will usually be the same.

In the case of PCBs, with respect to which further description will be directed, the amount of metal hydroxide present in the mix must be sufficient to essentially completely convert the chlorine content of the PCBs to the metal chloride salt, while the alkali metal nitrate must be present in sufficient amount to essentially completely oxidize the carbon and hydrocarbon content of the PCBs to a carbon oxide and water, and to cause salt precipitation and settling. Since the isomer mix can vary from situation to situation in the chlorination of biphenyl, it is desirable to analyze the PCBs so that appropriate hydroxide-nitrate quantities and mol ratios can be provided to effect the intended destruction and precipitation. The mol amount of nitrate should be substantially higher than that of the hydroxide to cause the salt to be readily precipitated and to settle out.

Reaction vessel 10 is heated by means of heating element 16 so as to convert the hydroxidenitrate mix to a molten bath which serves as the medium in which the destruction of the PCBs will take place. The temperature of the molten bath can range from a minimum of about 250° C. to as high as 800° C., or even higher. The exact temperature in any particular situation will be determined by the heat required to maintain the hydroxide-nitrate mix in a molten state without decomposition of either component, and by the heat required to carry out the destructive reactions of the PCBs. For most purposes, it has been found that a melt temperature of about 275° C. to 450° C. maintained in the reaction zone will be effective in attaining the desired destruction, when the PCBs are in the liquid phase in the melt.

Once the molten alkali metal hydroxide-alkali metal nitrate bath has been formed and the intended reaction temperature established, a stream of PCBs to be destroyed is introduced into reaction vessel 10 from storage tank 19. The normal physical form of PCBs may vary from liquids to solids of varying crystallinity depending upon the isomer mix. Any of these may be treated by the method of this invention in their normal physical form. For ease of injection into the molten bath the PCBs should be in a liquid form. Introduction of the PCBs into reaction vessel 10 is made preferably beneath the surface of the molten hydroxide-nitrate bath by injecting the liquid PCBs slowly into a flowing stream of air or oxygen.

As the PCBs are slowly added to the hydroxidenitrate melt, the destructive reactions commence. Alkali metal chloride is formed which is only partially soluble in the melt and which, if the nitrate concentration is high enough, precipitates toward the bottom of reaction vessel 10 from which it can eventually be withdrawn through salt discharge valve 18. Gaseous reaction products formed by the nitrate oxidation of the dechlorinated biphenyl residue accumulate in reaction vessel 10 and are passed through reflux condenser 22. Any condensate drawn off from reflux condenser 22 is returned as a reflux in toxic product feed column 21. Uncondensed vapors in reflux condenser 22, comprising principally carbon dioxide and water, are discharged to the atmosphere. The reaction time required to attain complete destruction of the PCBs, or other product, as the case may be, will vary from situation to situation depending upon the composition of the toxic product and the quantity of toxic product to be destroyed. The needed reaction time in each situation can best be established by simple tests.

During the destructive reactions of the PCBs, a stream of the molten bath, now containing alkali metal nitrite as a product of the nitrate reduction, may be withdrawn from the body of the bath and passed through nitrite oxidizing column 25. Alkali metal nitrate can be regenerated by contacting the stream of nitritebearing melt in nitrite oxidizing column 25 with preheated air introduced through air valve 29. The oxidized stream of melt now bearing at least some regenerated alkali metal nitrate is passed through demister 26 for removal of droplets, and is returned to reaction vessel 10 through toxic product feed column 21. Hydroxide is consumed by reaction with the toxic product, and should be replaced as needed. Although the nitrate can be regenerated in the bath, some is carried out as salt is removed. Replacement nitrate should therefore be added to maintain the desired proportions.

In order to provide better contacting, columns 13, 21 and 25 are desirably provided with baffle plates or agitating means as shown in the drawing. Use of motor driven agitating means (such as shown in column 13) is preferred.

Although not essential to the efficacy of the method of this invention, an oxidation catalyst such as ammonium molybdate can be incorporated in the hydroxidenitrate melt. Similarly, injection of air into the reacting hydroxide-nitrate melt can be continued after addition of the PCBs is completed for all or a part of the reaction period, to oxidize the nitrate that are formed.

FIG. 2 shows a presently preferred method for carrying out the method of the invention on a continuous or semi-continuous basis, with the toxic product in a gaseous phase. In this apparatus, which is not claimed herein and which is to be the subject of a separate patent application, the nitrate-hydroxide liquid mixture is contacted with PCB vapor in countercurrent flow relation. The nitrate and hydroxide are charged to a tank or reservoir 35 wherein they are initially melted by an external heat source means, i.e., a gas flame or heater tubes 33, to produce a liquid melt. The melt is then delivered from the reservoir 35 by a pump 36a, through a line 36, to the top of a reaction column 37. The lower end 34 of column 37 extends below the liquid level 51. The molten hydroxide-nitrate mixture is distributed over the internal cross-sectional area at the top of the column, as by a spray head 38, and makeup reagents are added through line 53 and trickles downwardly over a series of packing sections 40 in the column. These plates may comprise corrugated steel sheets. Desirably four vertically spaced packing sections 40 are provided. The toxic product is carried by an air stream in a line 41, and is supplied into column 37 near the lower end thereof, above the melt surface 51. The feed may comprise liquid droplets. This feed falls onto the melt, the temperature of which is above the boiling point of the material to be destroyed, so as to vaporize it. (The boiling points of PCBs are in the range of about 275°-500° C., depending on the particular compound.) The toxic product is vaporized, and it and the vapor of its decomposition products rise upwardly in column 37, in countercurrent flow to the falling streams of hydroxide-nitrate mixture. The composition of the reacting mass varies greatly along the column; the toxic product reacts near the bottom to form secondary organic products which then react in the higher packing sections. The nitrate and hydroxide concentration is high at the top of the column but becomes progressively lower toward the bottom. Once initiated, the destruction process is highly exothermic and large quantities of heat must be removed in order to maintain a steady temperature. Desirably this is carried out, as shown in the drawing, by cooling coils 45 between the respective packing sections 40. A coolant is passed through the coils 45 to maintain the reaction mass at the desired temperature level. If necessary, pump upflow line 36 can also be cooled.

The toxic product vapor reacts with the molten mixture in the packing section and produces salt which is carried downwardly in the column by the melt streams. Provided the proportion of nitrate in the tank is sufficiently high, the salt is precipitated and the particles settle out in the melt pool in the tank 35, to the bottom 46. The tank is provided with drag bar conveyor 48 which scrapes the salt particles from the bottom of the tank and sweeps them over an apron 49 for easy removal. The gaseous reaction products, i.e., carbon dioxide and water vapor, pass through a mist eliminator 52 and a vent 53 at the top of the column.

It is a highly desirable feature of the invention that the salt is segregated in the bath at the bottom and can be easily removed in crystal form. This avoids the accumulation of dissolved or suspended salt in the melt, and greatly facilitates continuous operation. It also insures that the concentration of reactants remains high, to drive the reaction toward completion.

By way of demonstrating the effect of a high proportion of nitrate in causing the reaction product salt to precipitate, the following series of comparative tests was run.

A. Salt was gradually added to a clear melt of $NaNO_3$ at a temperature of 400° C. When the salt content of the mixture reached approximately 6% (% by weight of the total) grains of salt were visible, indicating that the solubility limit of the salt was reached. The salt did not dissolve but remained as undissolved salt grains.

B. NaOH was added to the 6% NaCl melt of A. above, to provide a 3:1 mol ratio of $NaNO_3$ to NaOH. The viscosity of the melt did not change greatly, but the salt grains dissolved. This shows that salt is more soluble in a $NaNO_3$/NaOH melt than in $NaNO_3$ alone.

C. Salt was gradually added to the $NaNO_3$/NaOH/NaCl mixture of B. At about 14% NaCl, by weight of the total mixture, the solubility limit of the salt was again reached and the salt grains remained undissolved in the melt.

D. Salt was added to a 400° C. melt of $NaNO_3$ and NaOH in 5:1 mol ratio. The solubility limit of the salt was reached at only about 8%. This shows that the higher proportion of nitrate facilitates precipitation of a larger proportion of salt from the melt.

E. When the melt of D is cooled from 400° C. to about 350° C., the cloudiness of the melt increases, thus indicating further precipitation of the salt from solution. When the malt is cooled to about 275°, it becomes thick and grainy, indicating heavy salt precipitation. This indicates the desirability of cooling the melt containing the reaction product salt, in order to facilitate its precipitation. For this reason it is preferred to run the destruction reaction at about 400° C., then to cool the melt containing the salt to assist in salt precipitation.

F. If a salt crystal growth promoting agent such as manganese dichloride, $MnCl_2$, is added to the melt, viscosity is reduced, salt crystals grow and settle out still more readily. It is known that manganese salts such as the dichloride, as well as lead and cadmium salts, will assist in the precipitation of salt from water (see *Kirk*

Othmer, 2d ed. Vol 18, p 480), but so far as is known such agents have not heretofore been used to assist in the precipitation of salt from molten solutions.

The method of this invention is further described by the following Examples which are illustrative only and not intended to be restrictive. Unless otherwise indicated, all parts are by weight.

EXAMPLE 1

A mixture of 33.5 parts by weight (0.84 mol) of sodium hydroxide and 343 parts (4.0 mol) of sodium nitrate (corresponding to a $NaNO_3/NaOH$ mol ratio of about 4.8) were introduced into a closed steel reaction vessel equipped with a dip tube and a condenser. After the hydroxide-nitrate mixture has been converted to a molten bath by application of heat, 50 parts of polychlorinated biphenyl were introduced. This corresponds to a NaOH/PCB mol ratio of 1.1 and a $NaNO_3$/PCB mol ratio of 1.1. The PCB was fed beneath the surface of the molten bath by allowing it to drip slowly into a stream of nitrogen passing through the dip tube. The quantities of NaOH and $NaNO_3$ were in approximately 10% excess of that needed stoichiometrically to convert all the PCB to NaCl, CO_2 and water, however the nitrate was not regenerated by addition of external air during the reaction. PCB injection into the molten bath was continued over a period of about 30 minutes during which period the temperature of the bath was maintained at a temperature of 338° C.-340° C. Following completion of injection of the PCB, the temperature of the molten bath was raised to 345° C. and maintained at that temperature for one additional hour. The reaction vessel was then opened and the molten bath removed and allowed to solidify by cooling. 0.04 part of a brown, waxy material was removed from the resultant cake by washing with toluene. On analysis by gas chromatography, the waxy material was shown to contain 1000 ppm of PCB. This indicated a 99.99+% destruction of the PCB injected into the reaction vessel. The amount of NaCl formed in this reaction was inefficient to judge its solubility in the melt, but some graininess was evident, indicating incipient precipitation.

EXAMPLE 2

The procedure of Example 1 was repeated. 50 parts of an askarel comprised of 70% Monsanto Chemical Company AROCLOR 1254 brand of PCB and 30% of trichlorobenzene, was injected into the molten bath over a two hour period, using air instead of nitrogen as the carrier and purge gas in the dip tube. The air flow rate was 1 L./min., which was sufficient to reoxidize the nitrite formed. The average melt temperature was about 345° C. A temperature of 340° C. was maintained for an additional one hour after addition of PCB had stopped, after which the reaction vessel was opened and the molten bath removed and permitted to solidify. 0.155 part of a waxy substance was extracted by toluene washing from the resultant cake and was found, on analysis, to contain 9750 parts of PCB. This represented a 99.5% destruction of the PCB injected into the reaction vessel. The air stream helped to regenerate and maintain the proportion of nitrate.

EXAMPLE 3

The procedure of Example 1 was repeated except that 68.6 parts (0.81 mol) of sodium nitrate were used in the hydroxide-nitrate mix. This represented an approximate 1:1 nitrate to hydroxide ratio. 50 parts of the PCB-containing askarel were injected into the melt by means of an air stream over a period of one hour at a temperature of 270° C. The amount of $NaNO_3$ was less than that required stoichiometrically to convert the dehalogenated biphenyl secondary reaction product to CO_2. The hydroxide-nitrate molten bath temperature was maintained at 270° C. for an additional hour while the injection of air into the bath was continued. On separation of the molten bath and solidification, 2.55 parts of a light tan waxy substance were recovered which, on analysis, was found to contain 4.2% PCB. This represented a 99.78% destruction of the PCB injected into the reaction vessel. This example illustrates that less complete destruction is attained as temperature is decreased.

EXAMPLE 4

The procedure of Example 1 was repeated using 114.4 parts (1.35 mol) of sodium nitrate in the hydroxide-nitrate mix together with 0.18 parts of ammonium molybdate as a catalyst. The NO_3/OH ratio was about 1.6. 50 parts of the askarel were injected into the hydroxide-nitrate molten bath by means of an air stream. Injection time and subsequent reaction time totalled 6.5 hours at a temperature of 410° C. The salt did not precipitate, as its solubility limit was not exceeded. The solidified molten bath was white in color, exhibited no exudation, and no PCB could be washed from it. 5.75 parts of condensate collected from the condenser were found to contain 22 ppm of PCB on analysis. This represented a 99.995% destruction of the PCB injected into the furnace, but the $NaNO_3$ proportions used were too low for salt removal.

To show the criticality of using the hydroxide and nitrate together in the method of this invention, the following Examples 5 and 6 were conducted in which the nitrate and hydroxide components of the mix were used, in the absence of each other.

EXAMPLE 5

The procedure of Example 1 was repeated except that the molten bath consisted of 67 parts of sodium hydroxide together with 0.35 part of ammonium molybdate as a catalyst. The molten bath contained no alkali metal nitrate. Addition of 100 parts of PCB-containing askarel into the molten bath by means of an air stream was made over a period of 70 minutes while maintaining a temperature of 340° C. The injection of air was continued for an additional hour while continuing to maintain a 340° C. temperature. On opening the reaction vessel, it was found that the bath was substantially solid rather than liquid. Salt remained suspended in the melt. Grainy deposits of an orange-red color were found in the upper reaches of the reaction vessel. Deposits also partially blocked the condenser. 15 parts of condensate were collected from the condenser which, when analyzed, showed a PCB content of 29.6%. This represented a 91.1% destruction of the PCB injected into the reaction vessel, a level low as not to be useful in a practical sense.

EXAMPLE 6

The procedure of Example 1 was repeated except that the molten bath consisted of 312 parts of sodium nitrate together with 0.18 part of ammonium molybdate as a catalyst. The molten bath contained no alkali metal hydroxide. Addition of 50 parts of PCB-containing askarel into the molten bath by an air stream was made over a period of 1.75 hours while maintaining a temperature of 400° C. The injection of air was continued for

an additional hour while maintaining a 350° C temperature. On opening of the reaction vessel, the bath was found to be black with a carbonaceous substance. On solidification of the molten bath, a gummy exudate formed on the surface. On extraction with solvent, this exudate was found to contain substantial particulate carbon. The level of destruction of the PCBs was much lower than in Examples 1-5.

EXAMPLE 7

The procedure of Example 1 is repeated except that the hydroxide-nitrate mix comprises 33.5 parts of potassium hydroxide and 343 parts of potassium nitrate. All other conditions of Example 1 remain the same. Percentage of destruction of PCBs is essentially the same as that obtained in Example 1. This demonstrates that other alkali metals can be used instead of sodium.

The description of the method of this invention has thus far been directed principally to the destruction of polyhalogenated polyphenyls, and particularly to polychlorinated biphenyls with respect to which it has been found to be especially effective. The method of this invention is, however, equally applicable to the destruction of other toxic halogen containing products, as well as to the destruction of sulfur and phosphorus containing toxic products. Representative of these types of products are, dichlorodiphenyltrichloroethane (DDT); gamma hexachlorocyclohexane (LINDANE); ortho-4-bromo-2,5-dichlorophenyl-omethylphenyl phosphorothionate (LEPTOPHOS); hexachlorobenzene; 2,4-dichlorophenoxyacetic acid (2,4 D); 2,4,5-trichlorophenoxyacetic acid (2,4,5 T); 2,3,7,8tetrachlorodibenzop-dioxin (AGENT ORANGE); 2,2-dichloroethenyl dimethyl phosphate (DICHLOROPHOS); 0,0-dimethyl dithiophosphate of diethyl mercaptosuccinate (MALATHION); ethylene dibromide and other halogencontaining toxic organic products. The destruction of a phosphorous and sulfurcontaining toxic organic chemical compound is shown in the following example.

Example 8

The reaction vessel described in Example 1 was charged with 65 parts NaOH, 130 parts of $NaNO_3$, and 0.25 parts of ammonium molybdate. The mixture was melted and heated to 440° C. After temperature equilibration, 50 parts of Ortho Malathion 50 Insect Spray, 50% solution (Chevron Chemical Company) were added over a one-hour period. The reactor was opened and was found to contain partly solidified salts. Analysis of the salts showed a phosphate content of 2.98% (as P_2O_5) and a sulfate content of 11.8%. The S/P ratio of the salts was approximately the same as that of the Malathion, which indicated complete destruction.

It should be noted that a further advantage of the invention is that the reaction mixture is non-corrosive to steel, in contrast to a reaction mass which contains hydroxide but not nitrate. Inspection of the reaction vessel after use shows a shiny hard black oxide coating, without rusting or corrosion. This greatly reduces the cost of the reactor that would otherwise be required.

Having described the invention, what is claimed is:

1. In a method for destroying a toxic organic chemical product wherein said toxic product is contacted with a molten mixture of an alkali metal hydroxide and an alkali metal nitrate to form an alkali metal salt as a product of reaction with said hydroxide, an organic intermediate reaction product also being produced,

the improvement which comprises,

maintaining a mol ratio of said nitrate to said hydroxide in said molten mixture of at least 2:1, the proportion of said nitrate in said mixture further being sufficiently high to provide a low viscosity of said mixture so that a large portion of said alkali metal salt settles as solid salt particles to the bottom of said molten mixture,

reacting said organic intermediate rection product with said nitrate to form CO, CO_2, or a mixture thereof, and water, and

removing said solid salt particles from said molten mixture at the bottom thereof.

2. The method of claim 1 wherein the mol ratio of nitrate to said hydroxide is in the range of 2:1 to 5:1.

3. The method of claim 1 wherein the mol ratio of nitrate to said hydroxide to said toxic product is in the range of about 2:1:1 to about 5:1:1.

4. The method of claim 3 wherein said toxic organic chemical product is a polyhalogenated polyphenyl product.

5. The method according to claim 4 in which the polyhalognenated polyphenyl product is contacted in gaseous form with said molten mixture.

6. The method of claim 1 further wherein a portion of said nitrate is removed from the bottom of said molten mixture along with said solid salt particles, and

additional mitrate is added to maintain the proportion of said nitrate in said mixture sufficiently high that said solid salt particles continue to settle to the bottom of said molten mixture.

7. The method of claim 1 wherein said mixture is initially melted by heat from an external source, and wherein said mixture is thereafter maintained in molten condition by heat of reaction.

8. The method of claim 1 including the further step of removing heat of reaction from said molten mixture, as said destruction proceeds, to maintain a substantially constant temperature.

9. The method according to claim 1 in which the toxic organic chemical product has a substituent any of halogen, sulfur o phosphorous atoms.

10. The method according to claim 1 in which said molten mixture is at a temperature which is above the boiling point of said toxic product.

11. The method according to claim 1 in which said nitrate is reduced to the corresponding nitrite by reaction with said intermediate reaction product, and at least a portion of said molten mixture is contacted with a stream of oxygen-containing gas, to oxidize the nitrite back to the nitrate.

12. The method according to claim 1 in which additional alkali metal hydroxide and nitrate are added to the mixture to at least partially replace that which reacted in the destruction of said product.

13. The method according to claim 1 in which the mixture is cooled after said salt has formed therein, thereby further decreasing the solubility of said salt in the mixture and increasing its precipitation from said mixture.

14. The method according to claim 1 further wherein a salt crystal growth promoting agent is also present in said mixture, to promote growth of salt crystals in the molten mixture.

15. The method of claim 14 wherein said salt crystal growth promoting agent is manganese chloride.

* * * * *

INCINERATION TECHNOLOGY FOR THE DESTRUCTION OF CHLOROFLUOROCARBONS, HALONS, AND RELATED CHEMICALS

Prepared for:

CONFERENCE ON CFCs, HALONS, AND RELATED CHEMICALS
COLLECTION AND DESTRUCTION

Austin, Texas
23-24 June 1988

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1.0 INTRODUCTION

The problem of how to dispose of toxic chemicals has been an important environmental issue for over 50 years in the United States. Development of environmentally acceptable methods for disposal of these materials, however, has been fully addressed in the past 10 years as a result of pressure caused by such regulatory acts as the Resource Conservation and Recovery Act (RCRA) and the Toxic Substances Control Act (TSCA). One method that has found acceptance by the regulatory agencies for treatment of toxic and hazardous wastes is incineration coupled with air pollution control devices which remove acid gases and particulates that are formed in the combustion process.

This presentation presents an overview of the incineration technologies which are suitable for treatment of chlorofluorocarbons, halons, cyanides, organo-phosphates, and other related chemicals.

2.0 INCINERATION TECHNOLOGY OPTIONS

The incineration technologies best suited for these applications are rotary kiln (RK), fluidized bed combustion (FBC), and liquid injection (LI). Each of these technologies is currently being operated in commercial facilities for incineration of these types of wastes. Other emerging technologies that have not been used commercially but are capable of treating some of the wastes under consideration are electromelt, plasma arc, molten salt, and wet air oxidation. All of the technologies have relative advantages and disadvantages. Such factors as flexibility, reliability, operability, and cost must be considered in selecting the optimum incinerator technology.

2.1 Rotary Kiln

Rotary kiln incinerators are thermal treatment devices which utilize a rotating refractory lined cylinder as the primary combustion chamber for

combusting and/or devolatilizing solids. The major components of a rotary kiln system include a solids feed system, the rotary kiln, a secondary combustion chamber, and air pollution control devices. The kiln is operated at temperatures in the 1500-1800°F range with residence times of 1-2 seconds for gases and minutes to hours for the solids. Products of combustion from the kiln enter the secondary combustion chamber and are exposed to temperatures in excess of 2000°F with sufficient excess air and residence time to obtain the required destruction efficiency.

2.2 Fluidized Bed

Fluidized bed incinerators use a bed of granular material, such as sand, which is fluidized by the upflow of combustion air to create turbulence which enhances the combustion process. As waste material is injected into the bed, heat is transferred into the waste feed. As the waste material oxidizes, the energy released is transferred back into the bed material to provide preheat for incoming wastes. These units are operated at temperatures in the 1500-1800°F temperature range with residence times of 1-2 seconds for the products of combustion. The bed depth for most conventional fluidized bed combustors is 3 feet when not fluidized and 6 feet during actual operation. These systems are limited to wastes such as sludges and solids that have fairly uniform shapes and small diameters.

A variation in fluidized bed technology allows for the bed material to be circulated through the combustion chamber, collected, and returned to the bed. This is referred to as circulating bed combustion and offers some advantages over stationary bed units by allowing higher gas flows and utilizing more of the combustion chamber for destruction efficiency. Fluidized bed combustors offer high destruction efficiencies and do not require secondary combustion chambers. Use of limestone as the fluidizing media allows in situ removal of acid gases, thus minimizing the need for air pollution control devices.

2.3 Liquid Injection

Liquid injection involves spraying the waste into a refractory lined combustion chamber with air and auxiliary fuel. The secondary combustion chamber included in other incinerator technologies (i.e., rotary kiln and electric infrared furnace) is actually a liquid injection incinerator which provides additional residence time for the products from the primary combustion device. It is limited to waste streams that are liquids that can be atomized. The typical operating temperature is 2000-2200°F with residence times that are in the 1-2 second range. High destruction efficiencies are achieved, but solids and most sludges cannot be treated in a liquid injection incinerator.

2.4 Emerging Technologies

New technologies which can be used for the destruction of chlorofluorocarbons and related compounds are plasma arc, electromelt furnace, molten salt, and wet air oxidation. None of these is currently being used in commercial incineration facilities, but all have been proven operationally. These systems are limited in their application but do offer advantages for certain types of wastes.

Plasma arc systems offer a means of achieving extremely high temperatures for the destruction of compounds that are difficult to oxidize. The process involves introducing wastes into the discharge of a plasma arc torch where temperatures as high as 9000°F are achieved. The wastes are atomized and pass into the main reaction chamber where they recombine to form nonhazardous products of combustion.

The electromelt furnace and the molten salt are similar in their methods of heat transfer to the waste feed streams. Both use molten liquids to provide a high temperature for pyrolysis of the wastes. In the case of the electromelt furnace, electrical energy melts constituents that form a molten glass phase into which the waste materials are fed. The molten glass phase

produces a constant infrared heat flux at 2200°F to provide for the ignition and pyrolysis of the waste materials. Additional air is injected above the molten pool to provide for oxidation of the combustible materials. The molten salt incinerator operates under the same principle but uses a salt with a high melt point to provide the heat flux.

Wet air oxidation units use air dissolved in water at high pressures (500-3000 psi) to oxidize wastes than can be dissolved in the water. This reaction occurs at temperatures much lower than those required for thermal oxidation, usually in the 250-550°F range. This technology is limited to liquids, and the concentration of combustibles must be maintained at levels low enough to prevent excessive heat build-up in the water. Auxiliary fuel is minimized by cross heat exchange between the treated discharge and the inlet feed stream.

3.0 QUENCHING TECHNOLOGIES

Since virtually all incinerator applications involve treating wastes that will produce particulates and acid gases, flue gas treatment is required before combustion products can be discharged to the atmosphere. The process steps required to remove particulates and acid gases cannot be achieved at the temperatures required for oxidation. Therefore, a flue gas cooling step referred to as quenching is required.

Quenching technologies used to cool flue gas prior to flue gas treatment include air injection, evaporative cooling by water injection, and waste heat recovery. The quench step can have one or more stages which can employ combinations of the quench methods listed above. Important factors in the evaluation of a quench system include availability of quench medium, ease and reliability of operation, and cost of equipment.

3.1 Air Injection

Air injection involves the introduction of ambient air directly into the flue gas stream to provide direct contact cooling upon mixing of the two streams. This method is quite reliable and offers no inherent operating difficulties. It does have the disadvantage of requiring a large amount of quench medium relative to flue gas. In general, the flue gas is cooled from temperatures in the 2200°F range down to the 170°F range. This means that the air will be heated from about 70°F to 170°F, resulting in about 14 parts of cooling air being required for each part of flue gas. This large increase in mass flow will require all of the downstream air pollution control equipment to increase in size to accommodate the added flow.

3.2 Evaporative Water Cooling

This method of quenching is also accomplished by direct contact with the hot flue gas. Water is spray atomized into the flue gas stream and provides cooling primarily through vaporization of the water droplets. Although this method of injection requires additional energy in the form of hydraulic head and atomization media such as compressed air or steam, the quantity of quench medium required is greatly reduced because the heat of vaporization of the liquid provides the heat sink. Only about 0.5 part of water is required per part of flue gas to achieve the same level of quenching as outlined above with air injection. The injection of water does create the possibility of corrosion if acid gases are present in the flue gas stream. Proper design and material selection for the quench system can minimize the potential for corrosion. This method of cooling does not affect downstream equipment sizing to the extent that air injection does and, in general, is more economical.

3.3 Waste Heat Recovery

For the other methods of quenching discussed above, the energy expended to obtain the temperature necessary for the required destruction

efficiency in the incinerator was lost out the stack. To maximize energy utilization, a waste heat boiler can be used to provide flue gas cooling and to generate usable energy in the form of steam. The major disadvantage is the potential for corrosion and plugging due to corrosives and particulates present in most incineration flue gas streams. Care must be taken in the design of the waste heat recovery system to minimize these potential sources of operational difficulties. Preconditioning by air injection to solidify molten salts is often used in conjunction with soot blowing to minimize fouling of the boiler tubes. Proper design and material selection can minimize the potential for corrosion. The cost of the equipment is greater for this method than for air or water quench, but waste heat recovery is the most economical method because of the recovery of usable energy.

4.0 AIR POLLUTION CONTROL TECHNOLOGIES

The flue gas treatment system for an incineration process should provide for the removal of particulates, acid gases, and heavy metal contaminants. Since much of the particulate matter in the flue gas stream was formed by condensation of constituents that were in the vapor state at the operating temperature of the incinerator, the resulting particle size distribution will be mostly in the micron to sub-micron range. Because acid gases tend to form aerosols upon condensing, the technologies suited for particulate removal must be able to remove sub-micron particulates including aerosols formed as the flue gas is cooled. The technologies which are proven for these applications include both wet and dry techniques. Dry removal methods include electrostatic precipitators and fabric filters or baghouses. Wet methods include packed bed scrubbers, venturi scrubbers, and wet electrostatic precipitators. Their use is categorized in Table 4-1.

TABLE 4-1. AIR POLLUTION CONTROL TECHNOLOGIES

Technology	Pollutants Controlled		
	Particulates	Acid Gases	Metals
ESP (wet)	1	1	2
Venturi Scrubber	1	1	1
Packed Bed Scrubber	3	1	3
Baghouse	1	2	1
Sorbent Injection	3	1	3

1-prime removal technology
2-secondary removal technology
3-not applicable

4.1 Wet Electrostatic Precipitators

Wet electrostatic precipitators use electrically charged plates to collect liquid droplets that are passed through an electrical field and separate them from the flue gas stream. These devices must operate at low gas velocities in order to achieve the separation. As a result, the pressure drop across the ESP is quite low when compared to other methods of removal. The main disadvantage, however, is the fact that ESPs are large vessels requiring increased capital costs. When exposed to acid gases in the flue gas stream, potential for corrosion is increased. The wet system is utilized to remove acid gases from the flue gas, but requires special materials of construction due to the corrosive environment.

4.2 Fabric Filters (Baghouse)

Fabric filters, commonly referred to as bag filters or baghouses, collect particulates from the flue gas by allowing the dust-laden gas to pass through a fabric sock which provides surface area to filter out the particulates. Bag materials limit the use of this technology to a maximum temperature of 400°F. Bag filters offer high removal efficiencies with low to moderate pressure drops. Particulates are removed by pulsing the bags with a back flow of compressed air or by actually reversing the flow through the bags to dislodge the collected particles. The major disadvantages of this method of removal are the possibility of bag rupture allowing particulate emissions and the exposure to corrosion of the casing by acid gas dew point corrosion.

4.3 Venturi Scrubbers

Venturi scrubbers are wet scrubbing devices that provide for the removal of particulates by intimate contact with a liquid stream. The flue gas stream is accelerated through the throat of the venturi. The high velocity gas stream atomizes the liquid into small droplets which are penetrated by the particulates. The entrapped particles in the liquid droplets are coagulated and recovered from the flue gas stream. This method requires high pressure drops relative to dry removal methods such as ESPs and bag filters. The main advantages are its low capital investment, high degree of reliability, and ease of operation. This type of scrubber will also remove acid gases if they are present in the flue gas.

4.4 Packed Bed Scrubbers

Packed bed scrubbers utilize a packing material to provide contact surface for absorption and neutralization of acid gases. The exhaust gases from the incinerator are cooled to saturation and then flow up through the packing material. A liquid reagent is introduced at the top of the scrubber and flows countercurrently down over the packing. Acid gases are absorbed

into the liquid and neutralized by a chemical reaction with the reagent. This method of scrubbing achieves high removal efficiencies with low to moderate pressure drops. Material of construction must be chosen that are compatible with the acids that may be formed if they are not totally neutralized by the reagent.

4.5 Sorbent Injection (Semi-dry Scrubbing)

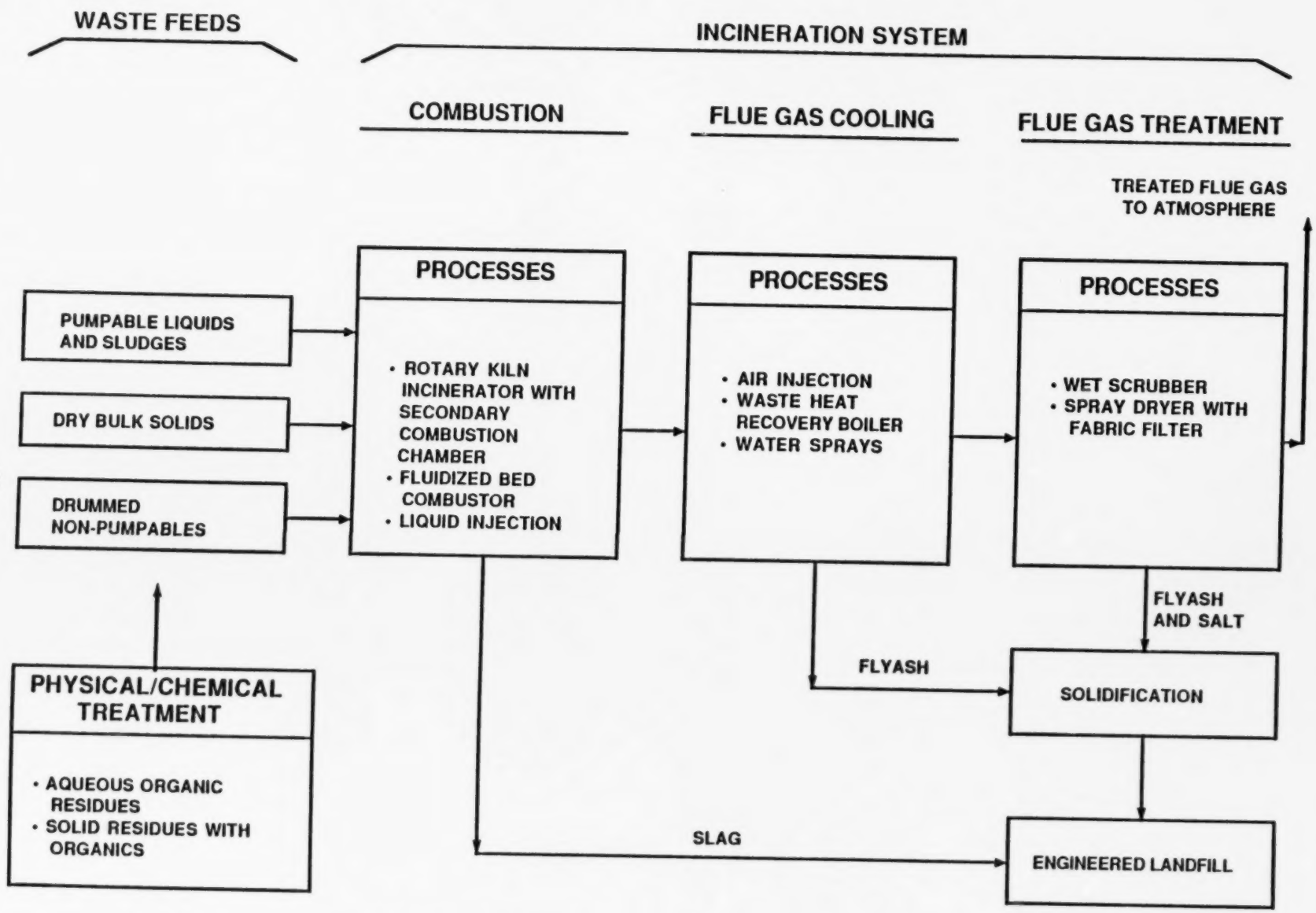
Sorbent injection involves the injection of a solution or dry reagent to adsorb and neutralize acid gases in the gas stream. It is usually injection by spray atomization if in solution form, rotating cup if a slurry, or pneumatic conveying if a dry solid. The temperature should be approximately 600°F for optimum removal efficiencies with the point of injection downstream of the incinerator. The resultant salt is recovered in a baghouse or ESP along with the removed particulates. The major advantage of this method is that acid gases are neutralized and their resulting salts are recovered dry without the need for additional equipment if particulate recovery is required. The main disadvantage is the limited removal efficiency compared with packed bed scrubbers.

INCINERATION TECHNOLOGY
for the
DESTRUCTION OF CHLOROFLUOROCARBONS, HALONS, AND RELATED CHEMICALS

Presented by

RADIAN CORPORATION

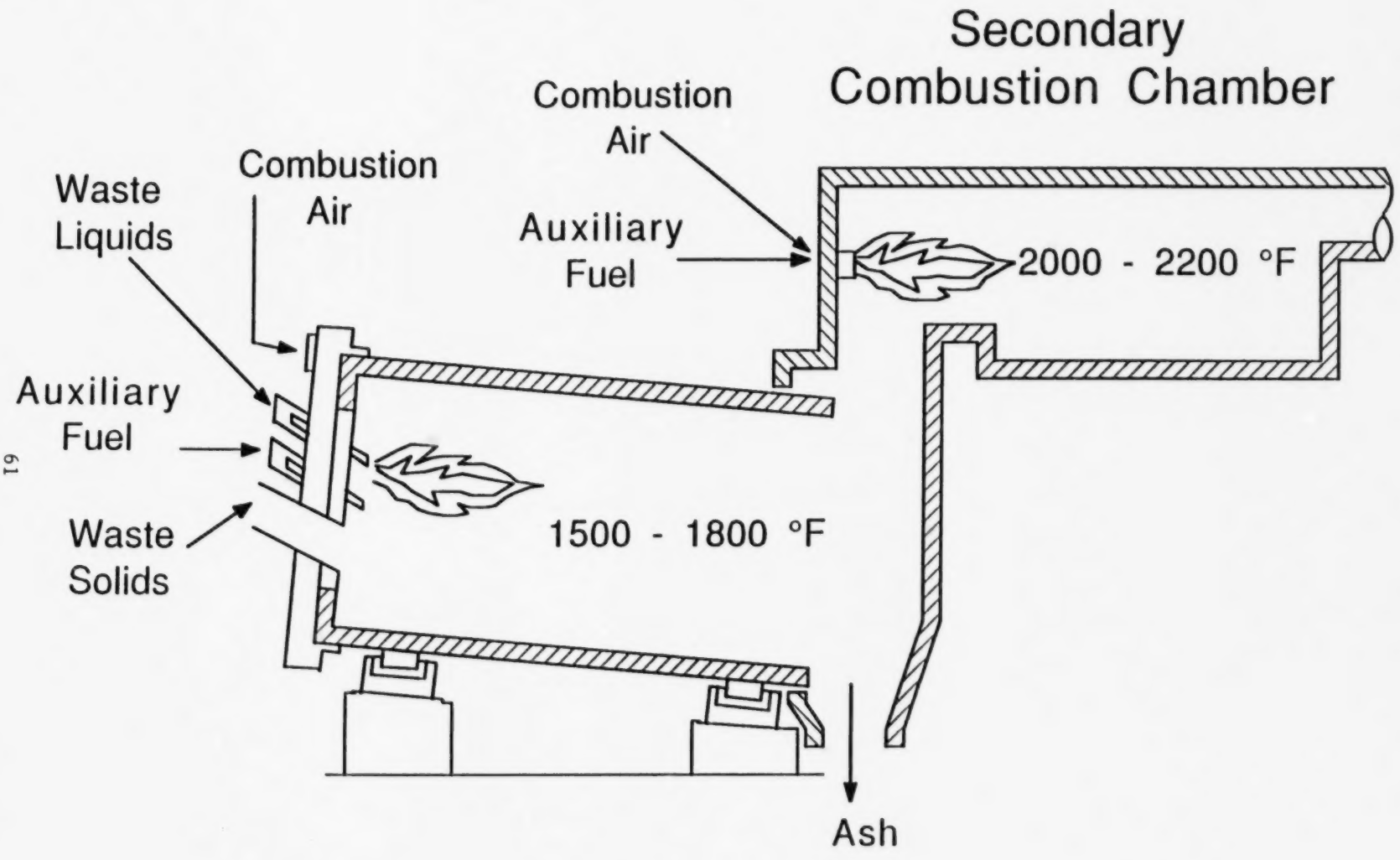
Ronald D. Bell



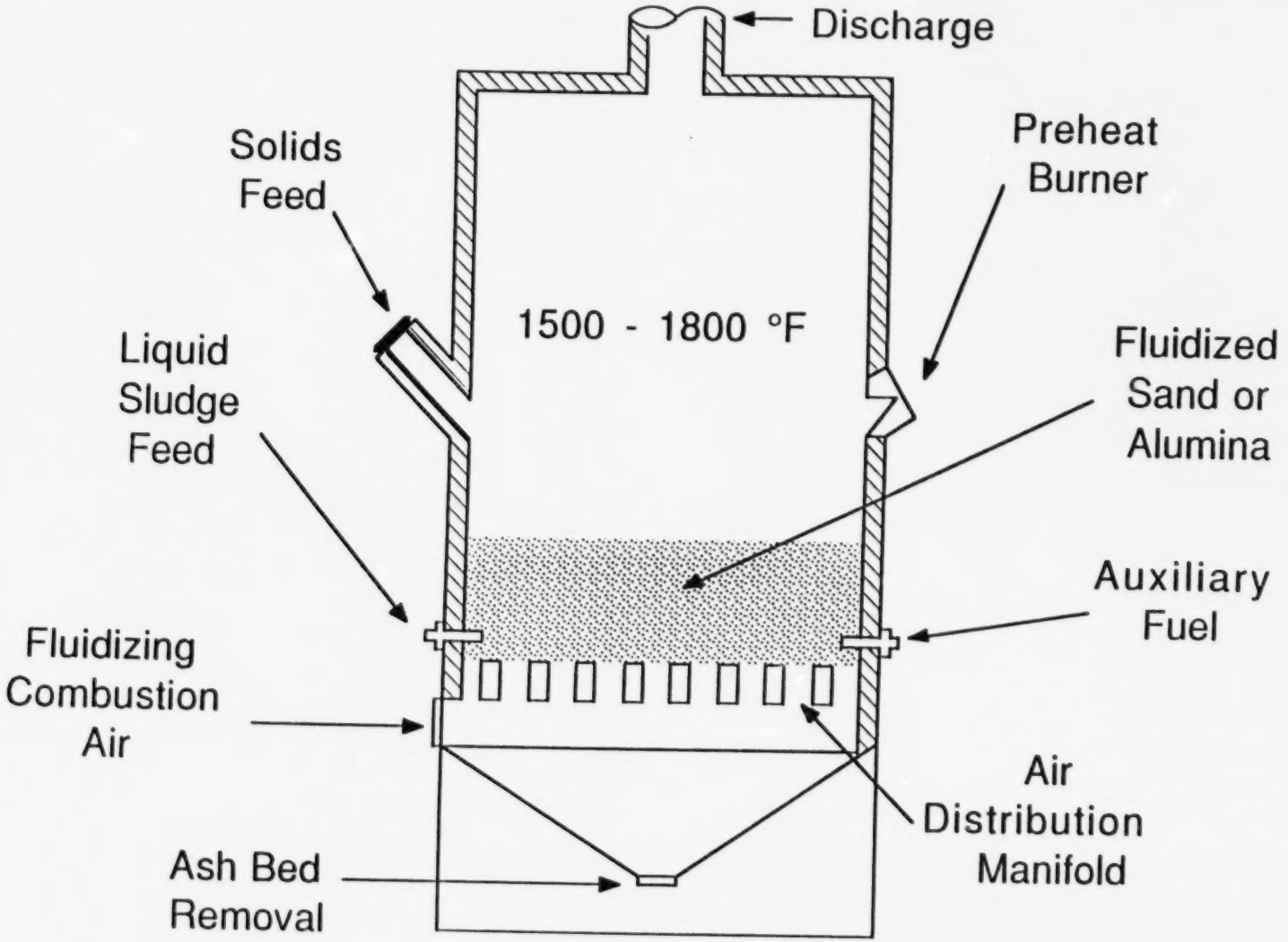
SCHEMATIC ILLUSTRATION OF INCINERATION SYSTEM

INCINERATION TECHNOLOGY OPTIONS

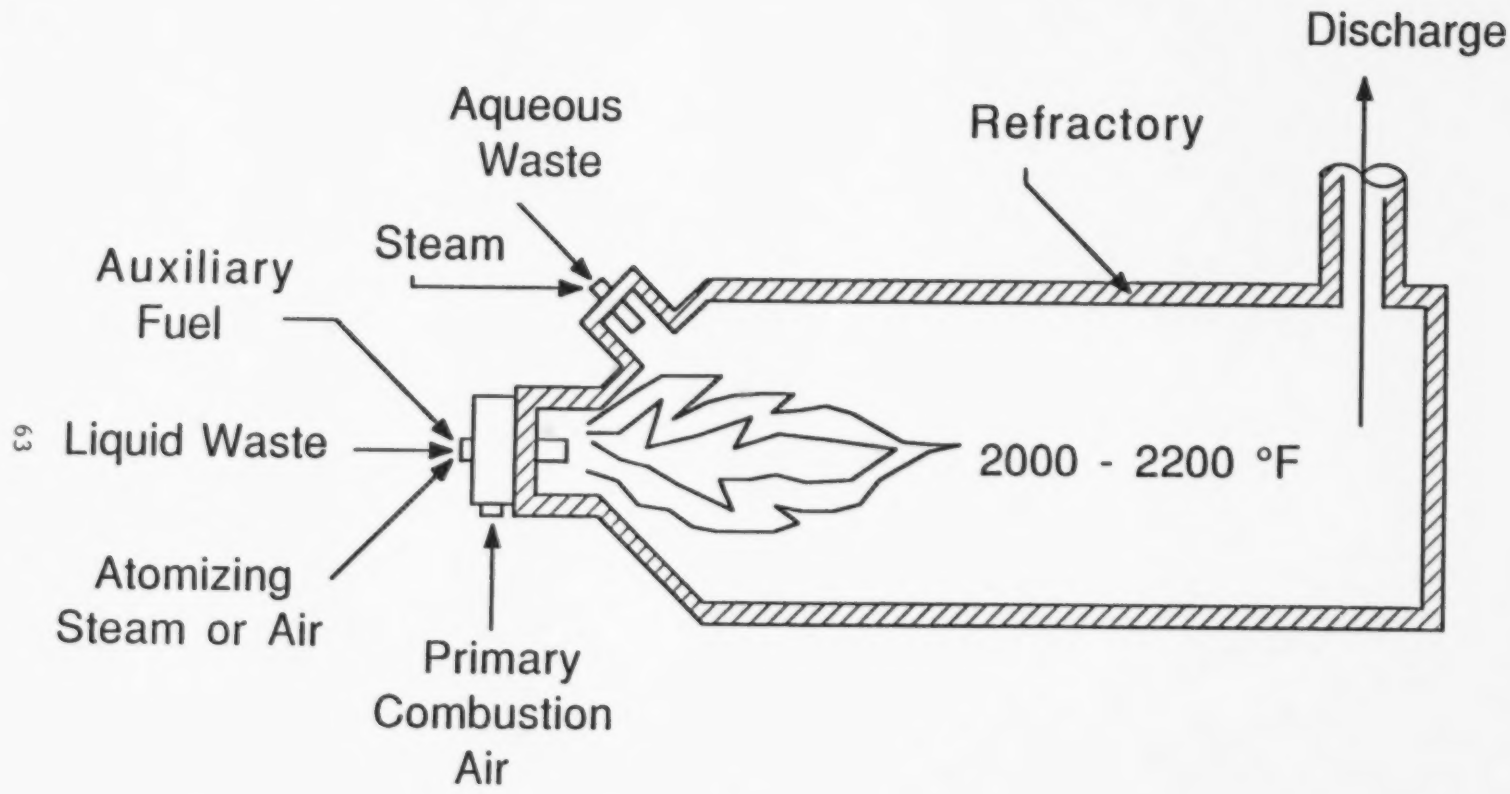
- Rotary kiln
- Fluidized bed
- Liquid injection
- Emerging technologies
  - plasma arc
  - electromelt
  - molten salt
  - wet air oxidation



Rotary Kiln Incinerator



Fluidized Bed Incinerator



Liquid Injection Incinerator

QUENCH TECHNOLOGIES

- Air injection
- Evaporative water cooling
- Waste heat recovery

AIR POLLUTION CONTROL TECHNOLOGIES

- Wet electrostatic precipitators
- Venturi scrubbers
- Packed bed scrubber
- Sorben injection (semi-dry scrubbing) with fabric filters (bag house)

AIR POLLUTION CONTROL TECHNOLOGIES

TECHNOLOGY	POLLUTANTS CONTROLLED		
	PARTICULATES	ACID GASES	METALS
ESP (Wet)	1	1	2
Venturi Scrubber	1	1	1
Packed Bed Scrubber	3	1	3
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Sorbent Injection	3	1	3

1 - prime removal technology
2 - secondary removal technology
3 - not applicable

Dr. David DeBerry, Radian Corporation

Chemical Treatment Methods

Oxidizing Agents

Low (ambient) temperature chemical or photochemical oxidation processes have been used to destroy a number of organic compounds.

Many 'high-powered' processes work mainly by generation of hydroxyl radicals, e.g.:

$$H_2O_2 + hv \longrightarrow 2\ {}^{\cdot}OH$$

$$O_3 + H_2O + hv \longrightarrow 2\ H_2O_2$$

$$O_3 + 2\ H_2O_2 \longrightarrow 2\ {}^{\cdot}OH + H_2O + 2\ O_2$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + {}^{\cdot}OH$$

However, even hydroxyl radicals may not be reactive with CFC's, as most of the mechanisms involve abstraction of a H atom or adding to an aromatic system or double bond. For a rough comparison, rate constants for reaction of several organic compound with ozone are shown below.

Compound	k ($M^{-1}sec^{-1}$)
benzene	2
methylene chloride	0.1
carbon tetrachloride	<0.005

The CFC's are most likely resistant to electrochemical oxidation except under extreme potentials in nonaqueous solvents.

Reagents and/or power sources are usually expensive for these processes.

Reaction with Active Metals

Halogenated hydrocarbons are known to react with metals such as sodium and potassium. Metals such as aluminum and zinc may also be fairly reactive.

An example reaction is:

$$3\ CCl_2F_2 + 8\ Al \longrightarrow Al_4C_3 + 2\ AlF_3 + 2\ AlCl_3$$

The aluminum carbide is said to decompose in the presence of water to give alumina and methane.

Cost of the active metals could be a consideration. For the above example the cost for aluminum alone is about $0.46/lb (CFC-12) if none of the aluminum can be recovered. CFC-12 costs about $0.68/lb.

Would need to remove water, oxygen from waste streams. Materials of construction could be a problem.

Thermodynamics of process need to be investigated.

Wet Air Oxidation

Uses high temperature (> 300 ^{o}C) aqueous stream and oxygen to destroy many organic compounds.

Oxidation will probably not be effective (for same reasons as given above), but combination with high temperature hydrolysis might give conditions similar to incineration (DuPont reference).

May be possible to catalyze process.

Thermodynamics of hydrolysis need to be investigated.

Corrosion

Destruction of CFC's can produce compounds which are corrosive to the equipment used for treatment.

Chlorides induce pitting and other forms of localized corrosion or stress corrosion cracking of many metals, including 'exotic' alloys.

Fluorides can attack materials which are resistant to chloride attack, eg: titanium. Ceramic materials (liners, etc) are susceptible to attack by HF and fluorides.

Potential corrosion problems should be considered when estimating the cost and the acceptability and reliability of the treatment processes.

CFC Summary

There a number of problems associated with chemical treatment methods for CFC's.

Thermodynamic calculations and directed literature surveys could clear up part of the uncertainty. Actual reactivities, degrees of conversion, kinetics would have to be determined experimentally.

Many fluoride salts are toxic and secondary disposal problems should be considered.

Possible corrosion problems and increased costs due to need for exotic materials of construction should be considered.

Since there are many fairly small sources of CFC's, it might be worth investigating processes whereby CFC's are adsorbed onto some support at the source, then transported to a central location for disposal (e.g., an incinerator).

CW Applications

Hydroxyl radical generating processes are quite applicable to most CW agents. Reactions are fast and complete. The reagents can be stored, but rapidly deployed.

Could also consider an adsorbent system which is periodically dosed with a strong oxidizing agent to make sure the surface is always 'active.'

BIODEGRADATION TECHNOLOGY

Presented by:

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What makes man-made organic compounds biodegradable?

Parameters to be fulfilled:

- Ability of microbial enzymes to metabolize compounds with structures similar to, but not identical with chemicals found in nature (fortuitous metabolism)
- Ability of man-man compounds to induce or derepress the synthesis of the necessary degradative enzyme(s) in microorganisms
- The presence of an appropriate environment (e.g., presence or absence of oxygen; the availability of nutrients; adequate pH; temperature; etc.)

Can microorganisms be used to destroy CFCs?

Problems:

- Halogenation increases the recalcitrance of organic compounds to biodegradation (e.g., methane vs. dichloro-difluoromethane; biphenyl vs. polychlorinated biphenyls)
- Volatility low boiling point of many CFCs
- Slow degradation rates compared to other technologies (no publications on CFC biodegradation)
- No advantages except for possible restoration of contaminated soil and water

How do microorganisms transform halomethanes?

- Studies primarily with chlorinated methanes (methyl chloride, methylene chloride, chloroform, carbon tetrachloride)

$$H \overset{?}{>} F > CL > BR$$

- Anaerobic and aerobic mechanisms reported

  Anaerobic = reductive dehalogenations under methanogenic conditions

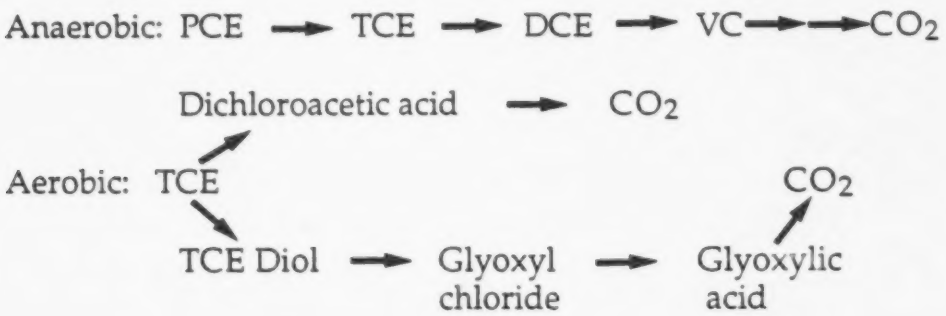
  Aerobic = Oxidative dehalogenations reported in soil & water microbes and in mammalian liver systems

- Cometabolic transformations. Energy for growth derived from other organic compounds

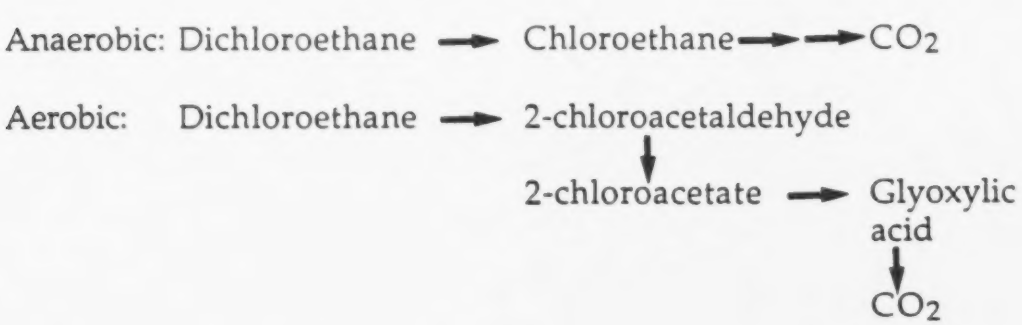
- Pathways not yet determined

How do microorganisms transform haloethanes and haloethenes?

- Studies primarily with chlorinated ethanes and ethenes
- Anaerobic degradation under methanogenic conditions. Aerobic degradation by methane oxidizing (methanotrophic) bacteria
- Cometabolic transformation
- Pathways for haloethenes:

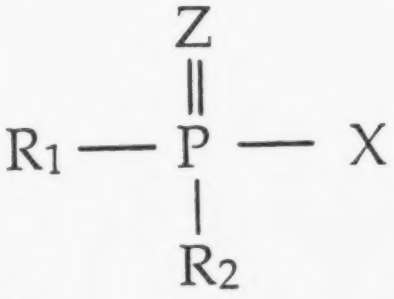


- Pathways for haloethanes:


Anaerobic: Dichloroethane → Chloroethane → → CO_2
Aerobic: Dichloroethane → 2-chloroacetaldehyde
2-chloroacetate → Glyoxylic acid
CO_2

Can microorganisms degrade chemical warfare agents?

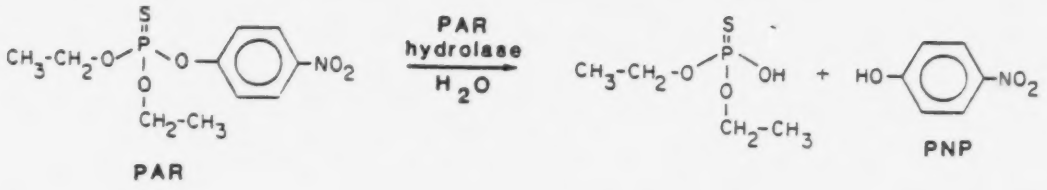
- HCN: Yes. Cyanide degraders are commonly found in soil and cyanide-containing industrial wastes
- Cyanogen chloride: ?
- Mustards: HD (sulfur mustard): Probably
  HN (nitrogen mustard): Probably
- Organophosphorous (nerve) agents: Yes



Z = Oxygen or sulfur
X = Easily displacable group (F, CN, SCH_2CH_2NR)
R_1, R_2 = Alkyl,alkoxy, or amino

Can microbial enzymes be used to hydrolyze G and V agents?

- DFP hydrolase from squid axon and bacteria
- Parathion hydrolase from pseudomonas



Are biotechnology methods useful for CW agent destruction?

- Yes, if soil and water remediation is required. Probably not if bulk disposal of CW agents is required
- Possible novel decontamination methods

SOLAR DESTRUCTION OF HALOCARBONS

Sandia National Laboratories

Solar Energy Department

Jim Fish
Rich Diver
Hugh Reilly

Sandia Laboratories

Solar Energy

AGENDA

SOLAR DESTRUCTION OF HAZARDOUS WASTES

- o Overview
- o Approach
- o Status
- o Planned Activities

SOLAR DESTRUCTION OF CFCs

- o Approach
- o Issues

SUMMARY

OVERVIEW

Objective

Use solar energy to destroy hazardous wastes.
Process must achieve:
- -High DRE
- -Cost Effectiveness

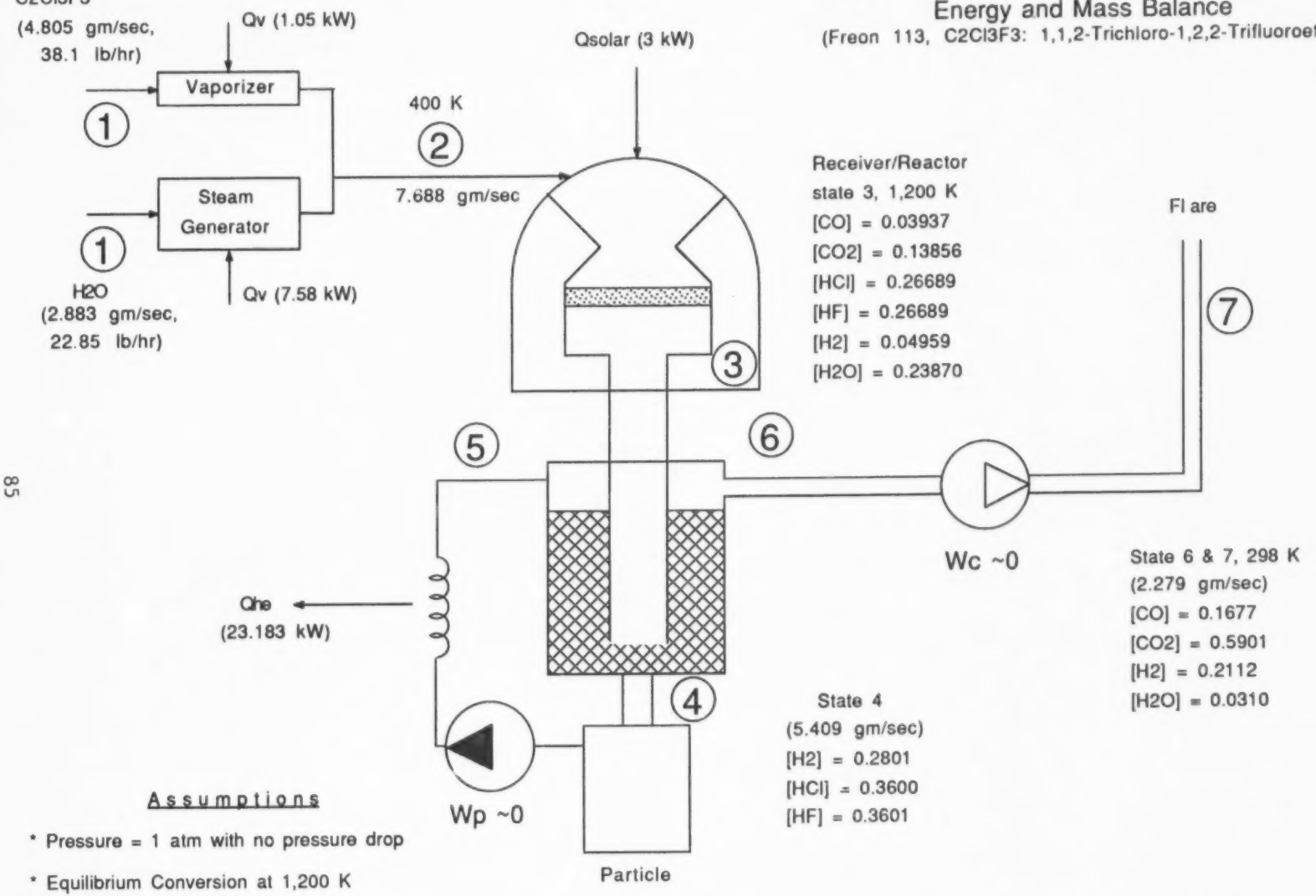
Scope

- -Direct Catalytic Absorption Receiver (DCAR) Development
- -Laboratory Experiments
- -Field Experiments
- -Modeling
- -Systems Analysis

APPROACH

- Catalytic Steam Reforming of Halocarbons
- Direct Catalytic Absorption Receiver (DCAR)
- Water Quench
- Neutralization of Acidic Product Gases

SOLAR DESTRUCTION OF HAZARDOUS WASTES
Energy and Mass Balance
(Freon 113, C2Cl3F3: 1,1,2-Trichloro-1,2,2-Trifluoroethane)



<u>Assumptions</u>

* Pressure = 1 atm with no pressure drop
* Equilibrium Conversion at 1,200 K
* Partial Pressure of water at 6 = 0.031 atm
* No CO2 dissolved in quench

WHY SOLAR?

COMBUSTION

- Fuel Required
- Oxygen Required
- Products of Incomplete Combustion
- NO_x
- Flue Gas Cleanup

SOLAR

- Concentrated Effluent
- Potential for High DRE at Lower Temperature
- NO_x Free
- Potentially Effective at Smaller Scale

STATUS

- Test Setup
- Test Results to Date

TEST RESULTS

Preliminary Tests Indicate Equilibrium Conversion of CO_2 / CH_4 and H_2O / CH_4

- Temperatures in the range 1000 - 1200K
- Pressures in the range 0.5 - 0.7 atm
- Solar power absorbed by chemicals in the range 1 - 4 kW
- Less than 1% CH_4 at outlet (in agreement with equilibrium predictions)
- Reactor matrix and catalyst not optimized

PLANNED ACTIVITIES

- Continued Testing to Include Chlorinated Hydrocarbons
- Conceptual Design of System for Chlorinated Hydrocarbons
- DCAR Reactor Modeling

APPROACH

- Catalytic Steam Reforming / Acid Neutralization
- Small-scale Material Compatibility Experiments
- Demonstrate at 3 kW Scale on Fresh CFC

Solar Destruction of CFCs

ISSUES

- Material Handling
  - o Hydrofluoric Acid
  - o Contaminants in Spent CFCs

- Proof-of-Concept Tests (Very Stable Compounds)

SUMMARY

- DEMONSTRATED PERFORMANCE ON HYDROCARBONS
  - o High Extent of Reaction
  - o 3-5 kW Level
  - o Achieved Matrix Temperature of 1300K

- CHLORINATED HYDROCARBONS NEXT

- FLUORINATED HYDROCARBONS NOT IN CURRENT SCOPE